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NEWS 5 JAN 28 MARPAT searching enhanced
NEWS 6 JAN 28 USGENE now provides USPTO sequence data within 3 days of publication
NEWS 7 JAN 28 TOXCENTER enhanced with reloaded MEDLINE segment
NEWS 8 JAN 28 MEDLINE and LMEDLINE reloaded with enhancements
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NEWS 14 MAR 31 IFICDB, IFIPAT, and IFIUDB enhanced with new custom IPC display formats
NEWS 15 MAR 31 CAS REGISTRY enhanced with additional experimental spectra
NEWS 16 MAR 31 CA/CAplus and CASREACT patent number format for U.S. applications updated
NEWS 17 MAR 31 LPCI now available as a replacement to LDPCI
NEWS 18 MAR 31 EMBASE, EMBAL, and LEMBASE reloaded with enhancements
NEWS 19 APR 04 STN AnaVist, Version 1, to be discontinued
NEWS 20 APR 15 WPIDS, WPINDEX, and WPIX enhanced with new predefined hit display formats
NEWS 21 APR 28 EMBASE Controlled Term thesaurus enhanced
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FILE 'CASREACT' ENTERED AT 11:09:20 ON 13 MAY 2008
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FILE CONTENT:1840 - 10 May 2008 VOL 148 ISS 20

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*
* CASREACT now has more than 13.8 million reactions
*

Some CASREACT records are derived from the ZIC/VINITI database (1974-1999) provided by InfoChem, INPI data prior to 1986, and Biotransformations database compiled under the direction of Professor Dr. Klaus Kieslich.

This file contains CAS Registry Numbers for easy and accurate substance identification.

=>
Uploading C:\Program Files\Stnexp\Queries\GH.str product

L1 STRUCTURE UPLOADED

=>
Uploading C:\Program Files\Stnexp\Queries\GH.str reactant/reagent

L2 STRUCTURE UPLOADED

=> S L1 FULL
FULL SEARCH INITIATED 11:10:08 FILE 'CASREACT'
SCREENING COMPLETE - 9102 REACTIONS TO VERIFY FROM 2415 DOCUMENTS

100.0% DONE 9102 VERIFIED 602 HIT RXNS 281 DOCS
SEARCH TIME: 00.00.02

L3 281 SEA SSS FUL L1 (602 REACTIONS)

=> S L3 AND LITHIUM METAL

25160 LITHIUM

51803 METAL

106 LITHIUM METAL

(LITHIUM(W) METAL)

L4 1 L3 AND LITHIUM METAL

=> S L3 AND LITHIUM
25160 LITHIUM

L5 86 L3 AND LITHIUM

=> S L3 AND LI
10305 LI

L6 59 L3 AND LI

=> D L4 IBIB ABS CRD 1

L4 ANSWER 1 OF 1 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 143:248504 CASREACT

TITLE: Method for producing alkyl lithium compounds and aryl lithium compounds by monitoring the reaction by means of ir-spectroscopy

INVENTOR(S): Weiss, Wilfried; Dawidowski, Dirk; Pleyer, Walter; Krueckel, Frank

PATENT ASSIGNEE(S): Chemetall G.m.b.H., Germany

SOURCE: PCT Int. Appl., 32 pp.

CODEN: PIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: German

FAMILY ACC. NUM. COUNT: 1

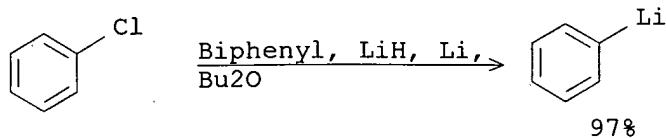
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 2005082911	A1	20050909	WO 2005-EP1954	20050224
W:	AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW			
RW:	BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG			
DE 102004009445	A1	20050929	DE 2004-10200400944520040227	
EP 1723153	A1	20061122	EP 2005-733858	20050224
R:	AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LI, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR			
CN 1922192	A	20070228	CN 2005-80005827	20050224
IN 2006CN03106	A	20070608	IN 2006-CN3106	20060825
US 20070152354	A1	20070705	US 2006-589715	20061023
PRIORITY APPLN. INFO.:			DE 2004-10200400944520040227	
			WO 2005-EP1954	20050224

OTHER SOURCE(S): MARPAT 143:248504

AB The invention relates to a method for producing alkyl lithium compds. and aryl lithium compds. by reacting lithium metal with alkyl or aryl halogenides in a solvent, the concentration of the alkyl/aryl halogenide and the alkyl/aryl lithium compound being detected according to an in-line measurement in the reactor by IR spectroscopy, and an exact recognition of the end point of the dosing of the halogenide constituents being carried out by evaluation of the IR measurement. Said method enables an optimum reactive process and reaction yield. The identification of the resp. concentration of the adduct and the product is a reliable reactive process. The yield of the reaction is also optimized by determining the end point of the halogenide dosing, as is the purity of the product due to a lower concentration thereof during the reaction.

RX(5) OF 5



CON: 4 hours, 35 deg C

REFERENCE COUNT: 1 THERE ARE 1 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

=> D L6 IBIB ABS CRD 1-59

L6 ANSWER 1 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 148:144945 CASREACT

TITLE: Remarkable β -Selectivity in the Synthesis of β -1-C-Arylglucosides: Stereoselective Reduction of Acetyl-Protected Methyl 1-C-Aryl-Glucosides without Acetoxy-Group Participation

AUTHOR(S): Deshpande, Prashant P.; Ellsworth, Bruce A.; Buono, Frederic G.; Pullockaran, Annie; Singh, Janak; Kissick, Thomas P.; Huang, Ming-H.; Lobinger, Hildegard; Denzel, Theodor; Mueller, Richard H.

CORPORATE SOURCE: Process Research and Development, Bristol-Myers Squibb, New Brunswick, NJ, 08903, USA

SOURCE: Journal of Organic Chemistry (2007), 72(25), 9746-9749
CODEN: JOCEAH; ISSN: 0022-3263

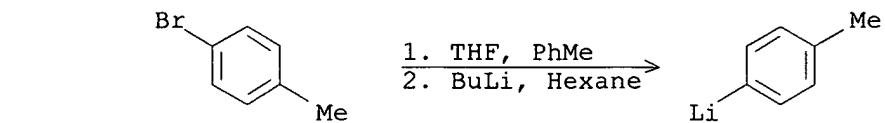
PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

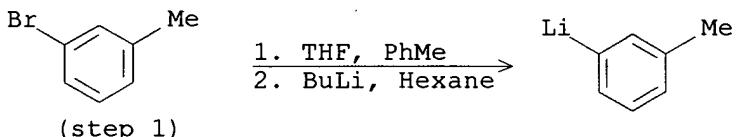
AB An efficient and practical process to generate β -C-aryl-glucoside derivs. was achieved. The process described involves Lewis acid mediated ionic reduction of a peracetylated 1-C-aryl Me glucoside derived from the addition of an aryl-Li to selectively protected δ -D-gluconolactone. The reduction of the 2-acetoxy-1-C-oxacarbenium ion intermediates proceeds with a high degree of selectivity to give β -C-aryl-glucosides without 2-acetoxy group participation. Furthermore, during the reduction process we also identified an unprecedented critical role of water. By changing from the usual benzyl ether protecting groups because of cost and chemical compatibility concerns, the new process is made addnl. efficient and highly selective.

RX(3) OF 39



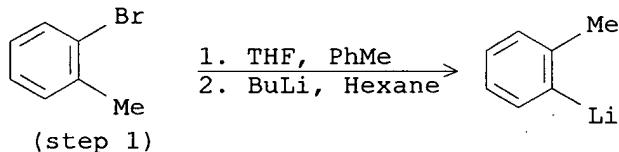
CON: STAGE(1) room temperature -> -78 deg C
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(5) OF 39



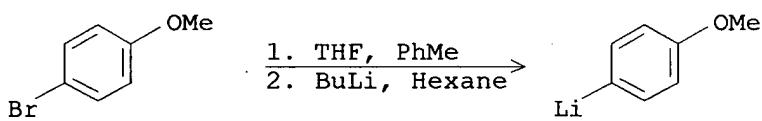
CON: STAGE(1) room temperature -> -78 deg C
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(7) OF 39



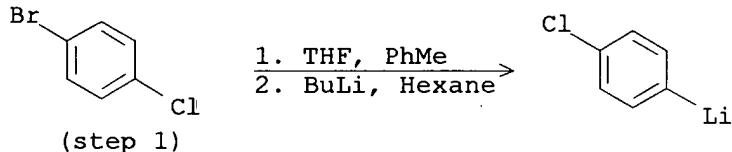
CON: STAGE(1) room temperature -> -78 deg C
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(9) OF 39



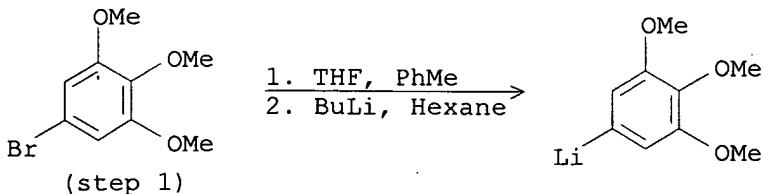
CON: STAGE(1) room temperature -> -78 deg C
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(11) OF 39



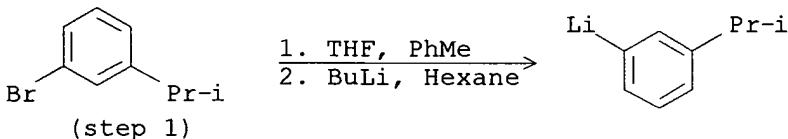
CON: STAGE(1) room temperature -> -78 deg C
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(13) OF 39



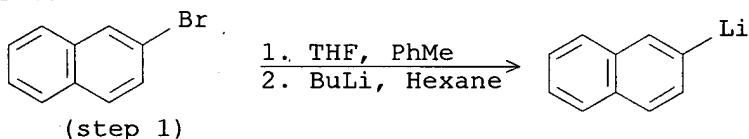
CON: STAGE(1) room temperature -> -78 deg C
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(15) OF 39



CON: STAGE(1) room temperature -> -78 deg C
STAGE(2) <-65 deg C; 1 hour, -78 deg C

RX(17) OF 39



CON: STAGE(1) room temperature -> -78 deg C
STAGE(2) <-65 deg C; 1 hour, -78 deg C

REFERENCE COUNT:

57 THERE ARE 57 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 2 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 147:406167 CASREACT

TITLE: The coupling of butylvinyltellurides with organometallic reagents catalyzed by nickel complexes

AUTHOR(S): Raminelli, Cristiano; Gargalaka, Joao; Silveira, Claudio C.; Comasseto, Joao V.

CORPORATE SOURCE: Instituto de Quimica, Universidade de Sao Paulo, Sao Paulo, 05508-900, Brazil

SOURCE: Tetrahedron (2007), 63(36), 8801-8809

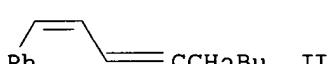
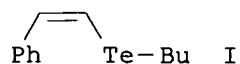
CODEN: TETRAB; ISSN: 0040-4020

PUBLISHER: Elsevier Ltd.

DOCUMENT TYPE: Journal

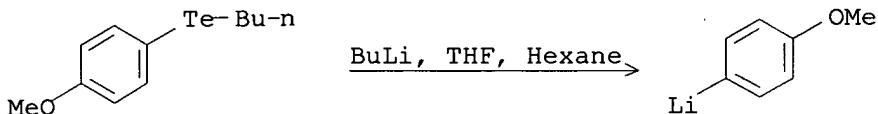
LANGUAGE: English

GI



AB Vinylic tellurides couple efficiently with sp, sp₂ and sp₃ hybridized organometallic compds. (Li, MgX and Zn species) in the presence of dichlorobis(triphenylphosphine)nickel(II) as catalyst. E.g., coupling reaction of (Z)-vinylic telluride I with 1-heptynyllithium, catalyzed by Ni(dppe)Cl₂, gave 100% (Z)-enyne II.

RX(23) OF 64



CON: 20 minutes, -70 deg C

REFERENCE COUNT: 66 THERE ARE 66 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 3 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 144:350731 CASREACT

TITLE: Co-complexes of ortho-dilithiated thiophenol or 2-trimethylsilylthiophenol with lithiated TMEDA molecules: synthesis, crystal structures and theoretical studies (TMEDA = N,N,N',N'-tetramethylethylenediamine)

AUTHOR(S): Hildebrand, Alexandra; Loennecke, Peter; Silaghi-Dumitrescu, Luminita; Silaghi-Dumitrescu, Ioan; Hey-Hawkins, Evamarie

CORPORATE SOURCE: Department of Chemistry, Babes-Bolyai University, Cluj-Napoca, RO-400084, Rom.

SOURCE: Dalton Transactions (2006), (7), 967-974

CODEN: DTARAF; ISSN: 1477-9226

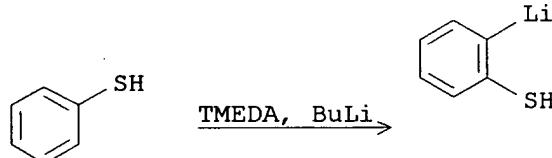
PUBLISHER: Royal Society of Chemistry

DOCUMENT TYPE: Journal

LANGUAGE: English

AB When an excess of BuLi was used in the ortho-dilithiation of thiophenol or 2-trimethylsilylthiophenol in the presence of TMEDA (TMEDA = N,N,N',N'-tetramethylethylenediamine), deprotonation of TMEDA occurred and crystals of [Li₃{(2-S-C₆H₄)(CH₂MeNCH₂CH₂NMe₂)}₂] (1) or [Li₄{(2-S-3-SiMe₃C₆H₃)(CH₂MeNCH₂CH₂NMe₂)₂(TMEDA)}] (2) were obtained. MO calcns. on gas-phase 1 and 2 at the DFT B3LYP/6-31G(d) level reproduce the exptl. structures fairly well. In spite of the short Li...cntdot.Li distances, total electron d. representations do not support the existence of Li...cntdot.Li interactions.

RX(4) OF 8



Li

94%

NOTE: regioselective, standard Schlenk technique used
CON: 0 deg C -> room temperature

REFERENCE COUNT:

56

THERE ARE 56 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 4 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 142:280267 CASREACT

TITLE: Synthesis and Structural Characterization of Lithium and Trimethyltin Complexes of 2,6-Bis(oxazolinyl)phenyl

AUTHOR(S): Stol, Marianne; Snelders, Dennis J. M.; De Pater, Jeroen J. M.; Van Klink, Gerard P. M.; Kooijman, Huub; Spek, Anthony L.; Van Koten, Gerard

CORPORATE SOURCE: Dutch Polymer Institute and Debye Institute, Department of Metal-Mediated Synthesis, and Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Utrecht, 3584 CH, Neth.

SOURCE: Organometallics (2005), 24(4), 743-749

CODEN: ORGND7; ISSN: 0276-7333

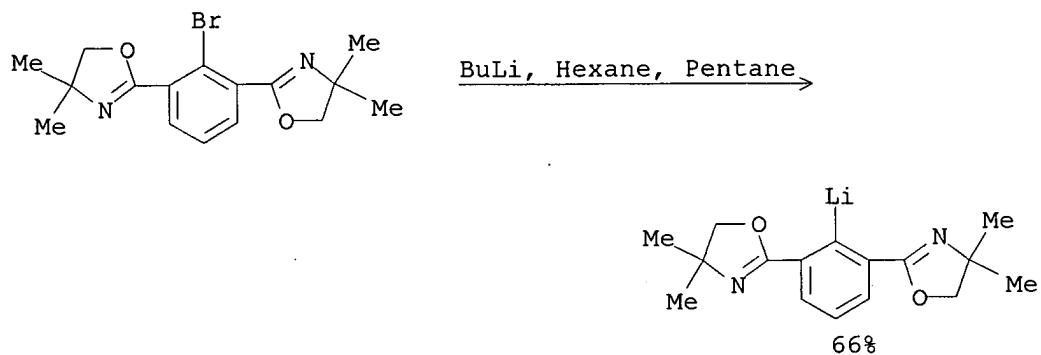
PUBLISHER: American Chemical Society

DOCUMENT TYPE: Journal

LANGUAGE: English

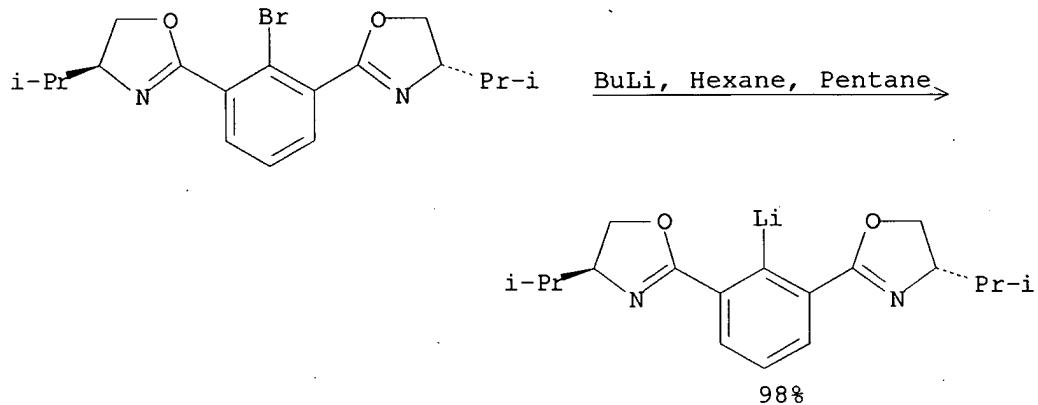
AB The treatment of 2,6-bis(oxazolinyl)phenyl bromide (Phebox-Br) with BuLi affords a Phebox-Li complex. Subsequent transmetalation with [SnClMe₃] affords a Phebox-Sn complex. The Phebox ligand can coordinate to a transition metal in various terdentate fashions; both the oxazoline O and the imine N are perfectly positioned for chelation; NCN, OCO, or mixed terdentate coordination modes are theor. possible using this ligand. The structural properties and NMR spectra of [Sn(Me,Me-Phebox)Me₃] (2) and [Li(R,R'-Phebox)] complexes 3a (R = R' = Me), 3b (R = iPr, R' = H), and 3c (R = tBu, R' = H) were studied. 2 Exhibits no chelation of the Phebox ligand to the Sn center in this case. The [Li(R,R'-Phebox)] complex 3a was crystallog. characterized and is as a mol. dimer (i.e. [Li(Phebox)]₂), containing two formally three-center-two-electron bonds in a four-membered Li₂C₂ ring. The formal Phebox anion is bonded to the Li cation via the two ortho imine N centers and the intraannular aromatic C atom. The ¹³C{¹H} NMR signal of Cipso, being a seven-line pattern with coupling constant J(13C-7Li) = 18 Hz, confirms that the dimeric structure is maintained in solution at room temperature. Variable-temperature (VT) NMR studies of 3a indicate that a fluxional process is occurring at room temperature, which can be frozen out <-16° (ΔG.thermod. = 56 kJ/mol). This fluxional process is not observed in VT-NMR studies on 3b,c. This is likely due to the presence of bulky (iPr or tBu) substituents that effectively shut down the pathways to rapid inversion of the puckering of the five-membered chelate ring.

RX(5) OF 11



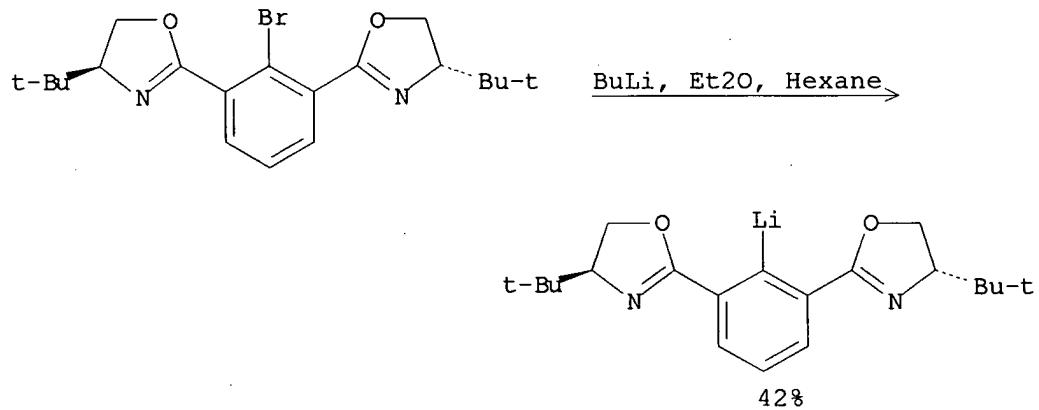
CON: STAGE(1) -78 deg C; -78 deg C → room temperature; 4 hours,
room temperature

RX(6) OF 11



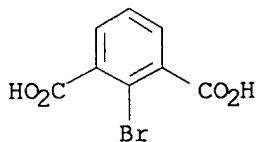
CON: STAGE(1) -78 deg C; -78 deg C → room temperature; 4 hours,
room temperature

RX(7) OF 11

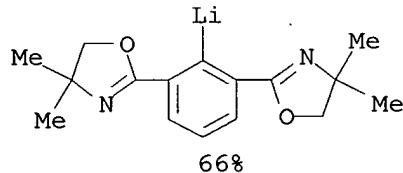


CON: STAGE(1) -78 deg C; 45 minutes, -78 deg C;
-78 deg C → room temperature; 3 hours, room temperature

RX(9) OF 11 - 2 STEPS

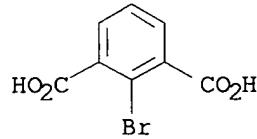


- 1.1. SOCl_2
- 1.2. $\text{HOCH}_2\text{CMe}_2\text{NH}_2$,
 Et_3N , CH_2Cl_2
- 1.3. CCL_4 , Et_3N , PPh_3 ,
 $\xrightarrow{\text{MeCN}}$
- 1.4. Water
2. BuLi , Hexane,
Pentane

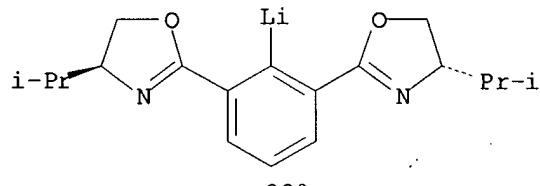


CON: STEP(1.1) overnight, reflux
 STEP(1.2) 0 deg C; overnight
 STEP(1.3) 0 deg C; overnight
 STEP(2.1) -78 deg C; -78 deg C \rightarrow room temperature; 4 hours,
 room temperature

RX(10) OF 11 - 2 STEPS

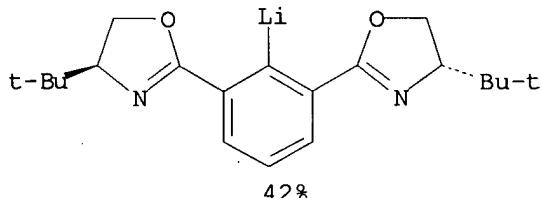
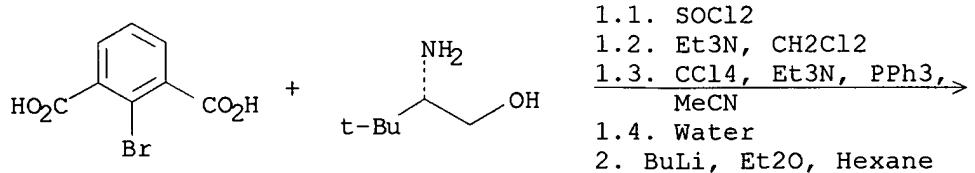


- 1.1. SOCl_2
- 1.2. (S)-Valinol,
 Et_3N , CH_2Cl_2
- 1.3. CCL_4 , Et_3N , PPh_3 ,
 $\xrightarrow{\text{MeCN}}$
- 1.4. Water
2. BuLi , Hexane,
Pentane



CON: STEP(1.1) overnight, reflux
 STEP(1.2) 0 deg C; overnight
 STEP(1.3) 0 deg C; overnight
 STEP(2.1) -78 deg C; -78 deg C \rightarrow room temperature; 4 hours,
 room temperature

RX(11) OF 11 - 2 STEPS



CON: STEP(1.1) overnight, reflux
 STEP(1.2) 0 deg C; overnight
 STEP(1.3) 0 deg C; overnight
 STEP(2.1) -78 deg C; 45 minutes, -78 deg C;
 -78 deg C -> room temperature; 3 hours, room temperature

REFERENCE COUNT: 43 THERE ARE 43 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 5 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 141:314360 CASREACT

TITLE: Preparation, thermal stability and carbonyl addition reactions of 2,5-difluorophenyl lithium and 2,5-difluorophenyl grignard

AUTHOR(S): Scott, Jeremy P.; Brewer, Sarah E.; Davies, Antony J.; Brands, Karel M. J.

CORPORATE SOURCE: Department of Process Research, Merck Sharp and Dohme Research Laboratories, Hoddesdon, EN11 9BU, UK

SOURCE: Synlett (2004), (9), 1646-1648
CODEN: SYNLES; ISSN: 0936-5214

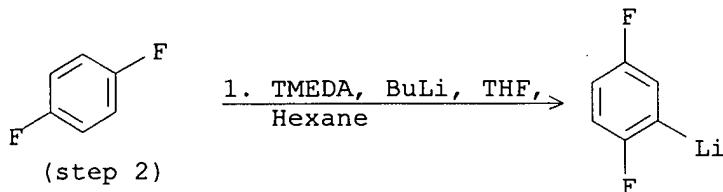
PUBLISHER: Georg Thieme Verlag

DOCUMENT TYPE: Journal

LANGUAGE: English

AB The generation of 2,5-difluorophenyl Li 2 by lithiation of 1,4-difluorobenzene with BuLi in THF, with and without amine additives, was surveyed. Thermal stability data of the organolithium species 2 generated with and without TMEDA were determined and the synthetic utility of 2 in the addition to aldehyde and ketone electrophiles is described. Preparation and stability of the corresponding organomagnesium reagent 1, generated by Br-Mg exchange of 1-bromo-2,5-difluorobenzene with isopropylmagnesium chloride, was also examined

RX(2) OF 9



CON: STAGE(1) 10 minutes, <-60 deg C; 10 minutes, -71 deg C
STAGE(2) 15 minutes, -71 - -68 deg C; 90 minutes,
-71 - -68 deg C

REFERENCE COUNT: 14 THERE ARE 14 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 6 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 137:63283 CASREACT

TITLE: Unusual structures of lithium terphenyl derivatives

AUTHOR(S): Hardman, Ned J.; Twamley, Brendan; Stender, Matthias;
Baldwin, Richard; Hino, Shirley; Schiemenz, Berthold;
Kauzlarich, Susan M.; Power, Philip P.

CORPORATE SOURCE: Department of Chemistry, University of California,
Davis, Davis, CA, 95616, USA

SOURCE: Journal of Organometallic Chemistry (2002), 643-644,
461-467

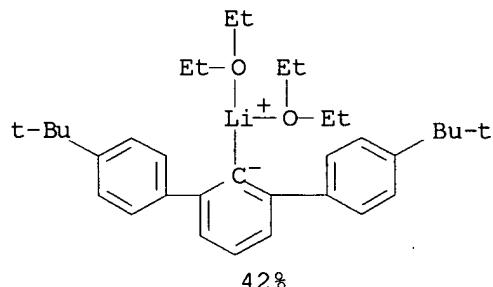
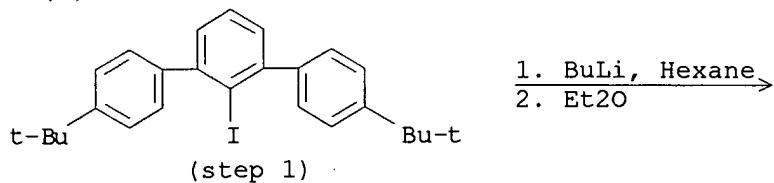
PUBLISHER: CODEN: JORCAI; ISSN: 0022-328X
Elsevier Science S.A.

DOCUMENT TYPE: Journal

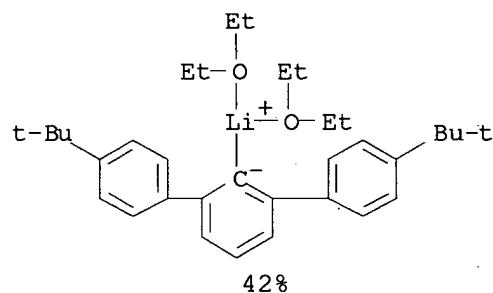
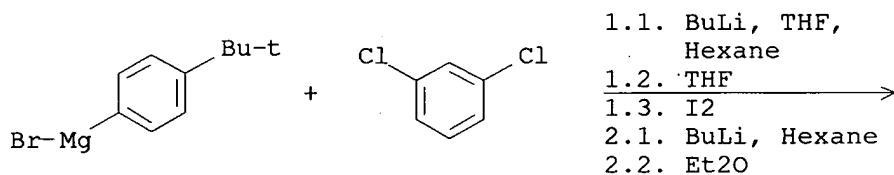
LANGUAGE: English

AB The synthesis, spectroscopic and structural characterization of three new Li derivs. of terphenyl ligands are reported. These are the mixed Li alkyl-Li aryl compound {Li(t-Bu)LiC₆H₃-2,6-Trip₂} (1, Trip = C₆H₂-2,4,6-i-Pr₃), the dilithiated {LiC₆H₃-2-(C₆H₃-2-Me-5-t-Bu)-6-(C₆H₃-2-CH₂Li-5-t-Bu)·Et₂O}₂ (2), and the ether solvated (Et₂O)LiC₆H₃-2,6-(C₆H₄-4-t-Bu)₂ (3). The synthesis of the terphenyl halide precursors for 2 and 3 is also given. The compound 1 resulted from the treatment of 1-BrC₆H₃-2,6-Trip with two equivalent of Li(t-Bu) in hexane. It features the alkyl and aryl (terphenyl) groups bridged by two Li ions. The Li ions are further solvated by ortho aryl substituents and methyls of the t-Bu groups. This compound is a very rare example of a mixed Li alkyl-Li aryl species. Compound 2 was obtained in low yield from the treatment of 1-BrC₆H₃-2,6-(C₆H₃-2-Me-5-t-Bu)₂ with two equivalent of Li(t-Bu). The terphenyl ligand was dilithiated by replacement of the Br and a H from one of the Me groups on the ortho aryl substituents. The ether solvated, dimeric, tetrametallic structure illustrated in the Table of Contents resulted. The compound 3 was obtained from the straightforward lithiation of the iodoterphenyl precursor in the presence of Et₂O and features a Li ion solvated by two ethers terminally bound to the ipso-C of the terphenyl group.

RX(3) OF 7



RX(7) OF 7 - 2 STEPS



REFERENCE COUNT:

21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 7 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 127:176492 CASREACT

TITLE: A simple one pot synthesis of 1-chlorophospholes

AUTHOR(S): Teunissen, Herman T.; Hansen, Carola B.; Bickelhaupt, Friedrich

CORPORATE SOURCE: Scheikundig Laboratorium, Vrije Univ., Amsterdam, NL-1081, Neth.

SOURCE: Phosphorus, Sulfur and Silicon and the Related Elements (1996), 118, 309-312

CODEN: PSSLEC; ISSN: 1042-6507

PUBLISHER: Gordon & Breach

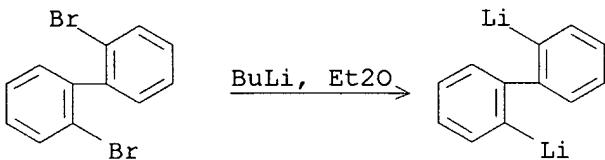
DOCUMENT TYPE: Journal

LANGUAGE: English

AB 1,4-Dilithio-1,2,3,4-tetraphenyl-1,3-butadiene, prepared from diphenylacetylene and Li, was cyclized with PCl₃ to give 57%

1-chloro-2,3,4,5-tetraphenylphosphole. Similarly, 2,2'-dibromobiphenyl gave 77% 5-chlorodibenzo[b,d]phosphole.

RX(2) OF 4



NOTE: 1 H, 20.deg.

REFERENCE COUNT: 13 THERE ARE 13 CITED REFERENCES AVAILABLE FOR THIS RECORD. ALL CITATIONS AVAILABLE IN THE RE FORMAT

L6 ANSWER 8 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 127:5187 CASREACT
 TITLE: Preparation of aryllithium in ether solutions using Lewis bases
 INVENTOR(S): Schwindeman, James A.; Sutton, Douglas E.; Morrison, Robert C.; Stryker, Sonia S.
 PATENT ASSIGNEE(S): FMC Corp., USA
 SOURCE: U.S., 4 pp.
 CODEN: USXXAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

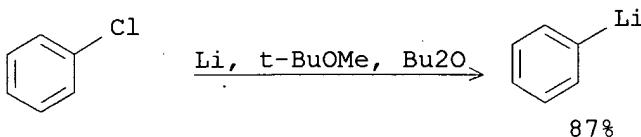
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5626798	A	19970506	US 1996-587813	19960105
WO 9725334	A1	19970717	WO 1996-US7624	19960524
W: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN				
RW: KE, LS, MW, SD, SZ, UG, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG				
AU 9658036	A	19970801	AU 1996-58036	19960524
DE 19681729	T0	19981217	DE 1996-19681729	19960524
DE 19681729	C2	20001116		
PRIORITY APPLN. INFO.:			US 1996-587813	19960105
			WO 1996-US7624	19960524

OTHER SOURCE(S): MARPAT 127:5187

AB An improved process for producing high purity solns. of aryllithium compds. and the product solns. are claimed. The process comprises reacting a particulate alkali metal having a particle size of 10-300 μm , with an aryl halide in a normally liquid ethereal solvent ROR₁, wherein R and R₁ are selected from the group of alkyl radicals containing from 3 to 6 C atoms, in the presence of a Lewis base selected from compds. of the formula: R₂AR₃(R₄)_z and cyclic -(CR₅R₆)_y-(A(R₄)_z)- wherein A is selected from O, N, P or S; R₂, R₃, and R₄ are selected from alkyl radicals containing from 1 to 6 C atoms; R₅ and R₆ are independently selected from H or alkyl radicals containing one to six C atoms; y = 4 to 6; but when A is O or S, z = 0; and when A is N or P, z = 1, and provided there is a mole ratio of ether to aryl halide of at least 1.3 to 1 and a mole ratio of Lewis base to aryl halide of from 0.01 to 0.5. For example, to a reaction flask containing 1.25 mol Li powder and 0.94 mol Bu₂O was added, dropwise, over a period of 60 min, a solution of 0.52 mol PhCl and

0.052 mol MeOtBu, while maintaining the reaction temperature at 30-35°; the yield of PhLi was 87.4%. If no MeOtBu was present, the yield was 80.8% and the reaction was slower (16% PhCl remaining after 120 min vs. 6%).

RX(1) OF 1



L6 ANSWER 9 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

123:284845 CASREACT

TITLE:

Lewis Acid-Induced Internal Proton Return in Enolate Complexes with Chiral Amines

AUTHOR(S):

Vedejs, Edwin; Lee, Namkyu

CORPORATE SOURCE:

Chemistry Department, University of Wisconsin, Madison, WI, 53706, USA

SOURCE:

Journal of the American Chemical Society (1995), 117(3), 891-900

CODEN: JACSAT; ISSN: 0002-7863

PUBLISHER:

American Chemical Society

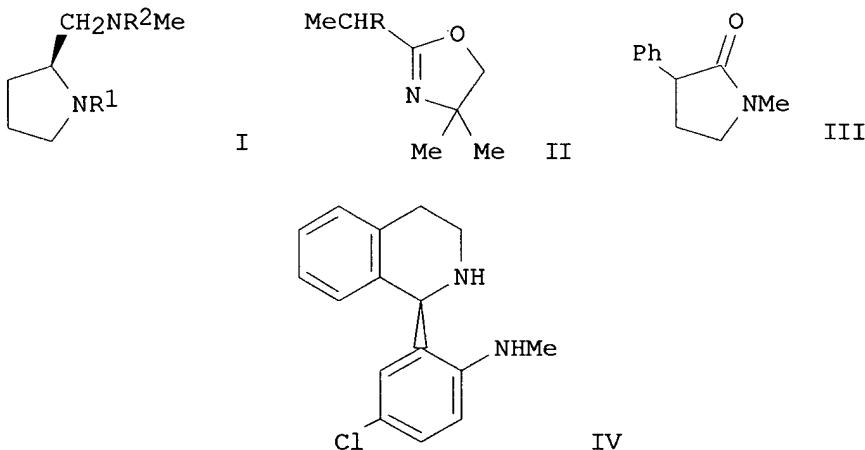
DOCUMENT TYPE:

Journal

LANGUAGE:

English

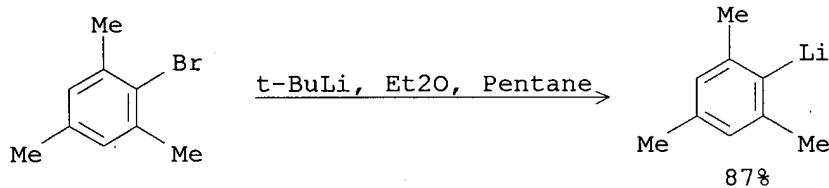
GI



AB Treatment of a 1:1:1 mixture of enolate $\text{RCMe:C(OLi)N(CHMe}_2)_2$ ($\text{R} = 6\text{-methoxy-2-naphthyl}$) (5), amine I [6; $\text{R1} = \text{H}$, $\text{R2} = \text{CH}_2\text{CH}_2\text{NMe}_2$], and lithium amide I ($\text{R1} = \text{Li}$, $\text{R2} = \text{CH}_2\text{CH}_2\text{NMe}_2$) with $\text{BF}_3\cdot\text{OEt}_2$ affords the naproxen amide $\text{RCHMeCON(CHMe}_2)_2$ (4a; same R) with an enantiomer excess of 77% ($>90\%$ yield). The result is attributed to Lewis acid-induced internal proton return (ipr) in a mixed aggregate containing the enolate and the chiral amine. Use of proline-derived diamines I ($\text{R1} = \text{H}$, $\text{R2} = \text{Me}$, Ph) in place of 6 affords 4a with 56-66% ee, but monoamines are relatively ineffective. Similar ipr conditions can be used to deracemize the oxazolidine II (same R) (50-60%), the lactam III (50% ee), and $\text{N,N-diisopropyl-2-(1-cyclohexenyl)propionamide}$ (62% ee). However,

disappointing results were obtained with several esters and α -(2-naphthyl)- γ,γ -dimethyl- γ -valerolactone (18). Lactone 18 was deracemized with the diamine IV (70% ee) under ipr conditions, but simple acyclic esters gave marginal ee values with IV ($\text{BF}_3\cdot\text{OEt}_2$ quench). Better results were obtained with Me N-benzoylalaninate (73% ee). In the latter case, the dianion was generated and ipr was induced by the sequential addition of IV and $\text{BF}_3\cdot\text{OEt}_2$ as before. In the case of amide 4a, ^1H NMR evidence shows that much of the proton transfer is complete before the addition of $\text{BF}_3\cdot\text{OEt}_2$ to the solution of IV and enolate 5. Thus, 5 is quenched by direct proton transfer, not by ipr, when 24 is used as the chiral amine. The proton transfer pathway can be correlated qual. with pK_a DMSO values. Thus, 24 was found to have a pK_a DMSO = 27.7 while the value for 4a is ca. 31. The relative acidity in THF is assumed to be similar, and 24 can protonate 5 directly but not the lactone enolate (18: pK_a (DMSO) = 20.1). Direct proton transfer does not occur with 6 (estimated pK_a DMSO = ca. 34-35) with any of the enolates studied and activation for ipr by $\text{BF}_3\cdot\text{OEt}_2$ is necessary to activate the N-H bond. In several examples, protic acid-induced ipr was also explored. In all cases, this gave lower ee values than the $\text{BF}_3\cdot\text{OEt}_2$ method.

RX(11) OF 28



L6 ANSWER 10 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 123:228304 CASREACT

TITLE: An efficient procedure for the synthesis of C-chiral bisphosphines

AUTHOR(S): McKinstry, Lydia; Livinghouse, Tom

CORPORATE SOURCE: Dep. Chem. Biochem., Montana State Univ., Bozeman, MT, 59717, USA

SOURCE: Tetrahedron (1995), 51(28), 7655-66

CODEN: TETRAB; ISSN: 0040-4020

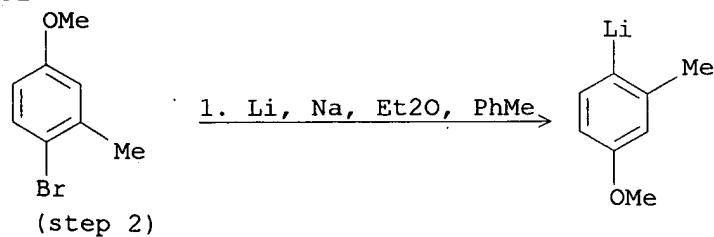
PUBLISHER: Pergamon

DOCUMENT TYPE: Journal

LANGUAGE: English

AB A practical method for the synthesis of bisphosphines containing homochiral C backbones, e.g., (2R,4R)-2,4-bis(dicyclohexylphosphino)pentane, is described. This procedure entails sequential reaction of a homochiral ditosylate, e.g., (2S,4S)-2,4-pentanediol di-p-toluenesulfonate, with the appropriate dialkyl- or diarylphosphine-borane anion, e.g., $\text{R}_2\text{P}\cdot\text{BH}_3\text{-Li}^+$ (e.g., $\text{R} =$ cyclohexyl, Ph) followed by BH_3 decomplexation mediated by $\text{HBF}_4\cdot\text{OMe}_2$.

RX(4) OF 92



L6 ANSWER 11 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

119:49043 CASREACT

TITLE:

Application of a copper(I)-mediated biaryl cross-coupling reaction to the synthesis of oxygenated 1,1'-binaphthalenes

AUTHOR(S):

Coleman, Robert S.; Grant, Eugene B.

CORPORATE SOURCE:

Dep. Chem. Biochem., Univ. South Carolina, Columbia, SC, 29208, USA

SOURCE:

Tetrahedron Letters (1993), 34(14), 2225-8

CODEN: TELEAY; ISSN: 0040-4039

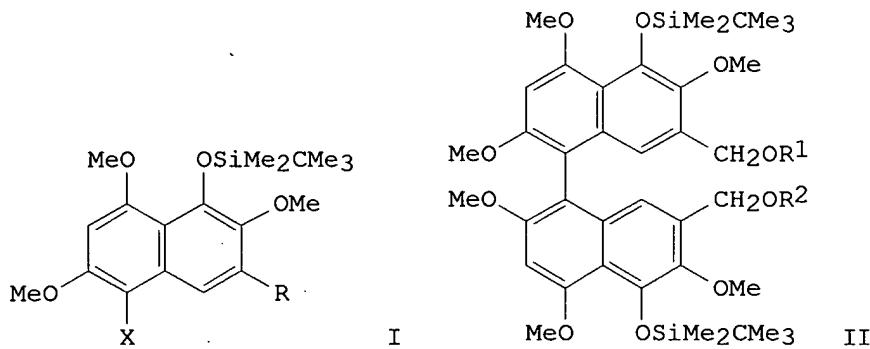
DOCUMENT TYPE:

Journal

LANGUAGE:

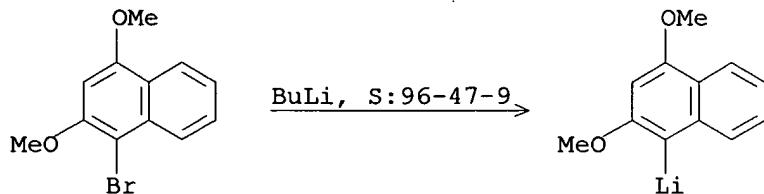
English

GI

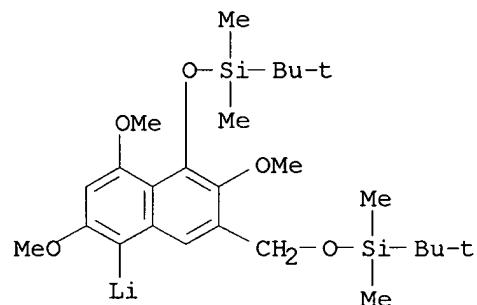
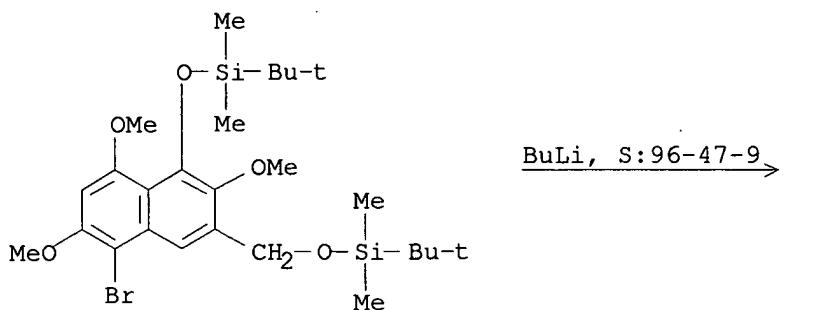


AB Application of an oxidative copper(I)-mediated biaryl cross-coupling protocol to the synthesis of highly oxygenated, differentially substituted 1,1'-binaphthalenes related to the perylenequinone calphostin C is detailed. Thus, coupling of naphthalene I ($R = CH_2OR_1$, $R_1 = SiMe_2CMe_3$, $X = Li$) with I ($R = CH_2OR_2$, $R_2 = SiPh_2CMe_3$, $X = CuCNLi$) gave binaphthalene II.

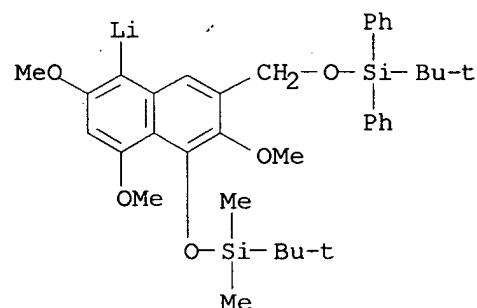
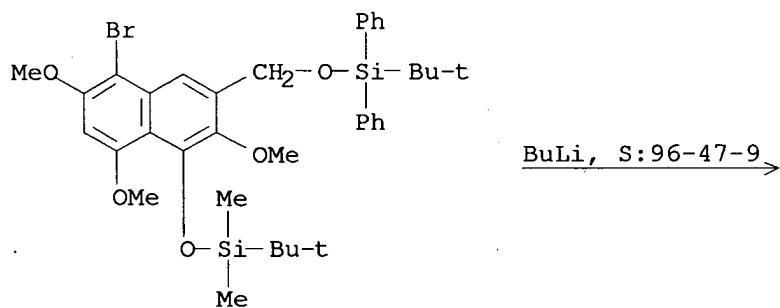
RX(1) OF 21



RX(5) OF 21



RX(6) OF 21



L6 ANSWER 12 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

118:102236 CASREACT

TITLE:

Preparation of aryllithiums in C6 dialkyl ether
solvents

INVENTOR(S):

Morrison, Robert Charles

PATENT ASSIGNEE(S):

FMC Corp., USA

SOURCE: PCT Int. Appl., 21 pp.

CODEN: PIIXXD2

DOCUMENT TYPE: Patent

LANGUAGE: English

FAMILY ACC. NUM. COUNT: 1

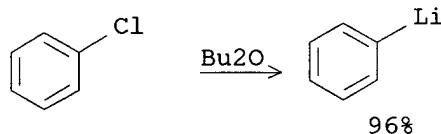
PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
WO 9219622	A1	19921112	WO 1992-US1208	19920214
W:	AU, BB, BG, BR, CA, CS, FI, HU, JP, KP, KR, LK, MG, MW, NO, RO, RU, SD			
RW:	AT, BE, BF, BJ, CF, CG, CH, CI, CM, DE, DK, ES, FR, GA, GB, GN, GR, IT, LU, MC, ML, MR, NL, SE, SN, TD, TG			
AU 9219262	A	19921221	AU 1992-19262	19920214
PRIORITY APPLN. INFO.:			US 1991-692438	19910429
			WO 1992-US1208	19920214

OTHER SOURCE(S): MARPAT 118:102236

AB Thermally stable solns. of aryllithium compds. were prepared by reaction of Li dispersions with monohaloaryl compds. in solvents ROR₁ (R, R₁ = C₃-8 alkyl; ≥6 carbons total) with a molar ratio of ether/monohaloaryl compound of ≥1.5 at a temperature of 5-65°. Thus, 1 equiv PhCl was added dropwise to a stirred slurry of Li in 1.8 equiv BuOBu followed by a postreaction period and filtration to give a .apprx.25% solution of PhLi which was stable for ≥40 days at 20-22°.

RX(1) OF 1



NOTE: product has improved stability in this solvent

L6 ANSWER 13 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 117:212546 CASREACT

TITLE: Dependence of the ability of 2-substituted thiophenes to inhibit reactions of organic halides with lithium on the electronic properties of substituents. Direct lithiation of 2-methylthiophene by butyl chloride and Li in ethyl ether

AUTHOR(S): Koikov, L. N.; Polikarpov, M. V.; Alekseeva, N. V.; Lisitsa, E. A.

CORPORATE SOURCE: Vses. Nauchno-Issled. Inst. im. Ordzhonikidze, Moscow, Russia

SOURCE: Metalloorganicheskaya Khimiya (1992), 5(3), 590-3
CODEN: MEKHEX; ISSN: 0235-0114

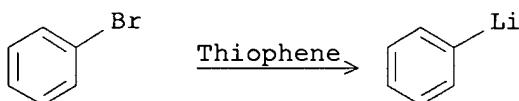
DOCUMENT TYPE: Journal

LANGUAGE: Russian

AB 2-Chloro- and 2-bromothiophene and selenophene inhibit the reaction of PhBr with Li in Et₂O similar to thiophene, while 2-methyl-, 2,5-dimethyl-, and 2,5-dichlorothiophene do not. In contrast to BuSH, PhCH₂SH, which gives an ether-soluble Li thiolate, is not an inhibitor. Formation of an unstable radical anion from a d-heterocycle that decomp. into an Et₂O-insol. Li thiolate or chalcogenide is presumed necessary for displaying the inhibiting properties. The difference in behavior of thiophene with donor (Me) and acceptor (Cl, Br) substituents, which have close steric characteristics, is accounted for by the inability of the former to give a radical anion. On the basis of the

data obtained, a preparative one-stage synthesis of 5-methyl-2-thienyllithium was developed from BuCl and Li in Et₂O. Subsequent carboxylation leads to 5-methyl-2-thiophenecarboxylic acid in 74% yield.

RX(1) OF 1



L6 ANSWER 14 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 117:69500 CASREACT

TITLE: Lithiation of (S)-(-)-N,N-dimethyl-1-phenylethylamine

AUTHOR(S): Dem'yanovich, V. M.; Shishkina, I. N.; Vedernikov, A. I.

CORPORATE SOURCE: Mosk. Gos. Univ., Moscow, Russia

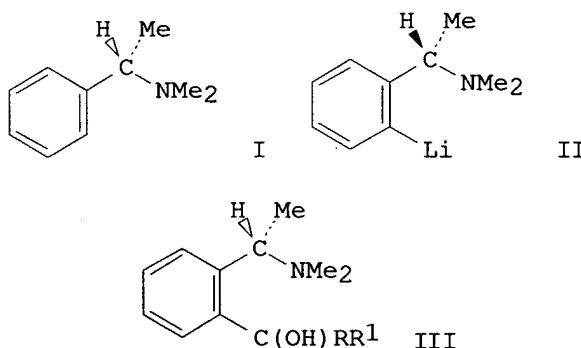
SOURCE: Zhurnal Organicheskoi Khimii (1991), 27(12), 2628-9

CODEN: ZORKAE; ISSN: 0514-7492

DOCUMENT TYPE: Journal

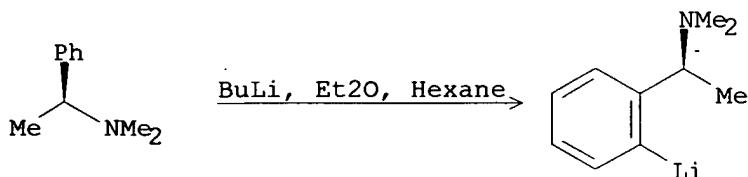
LANGUAGE: Russian

GI



AB Lithiation of benzylamine (S)-(-)-I by BuLi in Et₂O or hexane takes place only at the ortho position to give Li derivative II. Reaction of II with RR₁CO [R = R₁ = Ph, Me; R = H, R₁ = Ph; RR₁ = (CH₂)₅] gave 30-87% amino alcs. III.

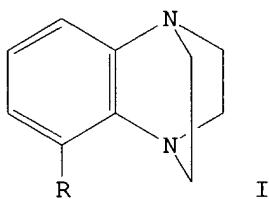
RX(1) OF 3



NOTE: Regioselective, either solvent

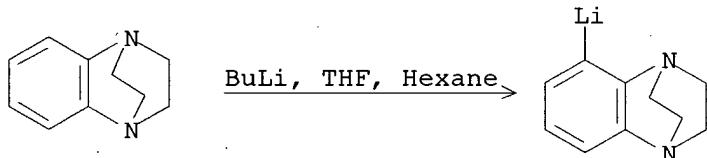
L6 ANSWER 15 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 116:21017 CASREACT
 TITLE: Diazabicycloalkanes with nitrogen atoms in bridgehead positions. 21. Heteroatom-promoted lithiation of benzo[b]-1,4-diazabicyclo[2.2.2]octene and introduction of substituents into the annelating benzene ring
 AUTHOR(S): Gall, A. A.; Trachum, A. S.; Romantsev, V. A.; Shishkin, G. V.
 CORPORATE SOURCE: Novosib. Inst. Bioorg. Khim., Novosibirsk, 630090, USSR
 SOURCE: Khimiya Geterotsiklicheskikh Soedinenii (1991), (6), 798-803
 DOCUMENT TYPE: CODEN: KGSSAQ; ISSN: 0453-8234
 LANGUAGE: Journal
 Russian
 GI



AB The lithiation of the title compound I ($R = H$) gave I ($R = Li$), the reaction of which with a no of electrophiles afforded derivs. I [$R = Br, I, CO_2H, OH, SiMe_3, B(OH)_3, CHO, 1\text{-hexylthio}$].

RX(1) OF 5

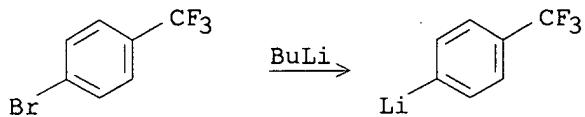


L6 ANSWER 16 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 113:211557 CASREACT
 TITLE: Preparation of α -[4-(trifluoromethyl)phenyl]benzenemethanols
 INVENTOR(S): Davidson, James G., III; Swierenga, Brian S.
 PATENT ASSIGNEE(S): Warner-Lambert Co., USA
 SOURCE: U.S., 6 pp.
 DOCUMENT TYPE: CODEN: USXXAM
 Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 4940822	A	19900710	US 1988-267428	19881104
PRIORITY APPLN. INFO.:			US 1988-267428	19881104
OTHER SOURCE(S): MARPAT 113:211557				
AB 4-(F3C)C6H4CH(OR)C6H4R1 ($R = Li, H; R1 = H, \text{halo, (halo)alkyl, aryl, etc.}$) are prepared by combining 4-(F3C)C6H4Br and BuLi reagent streams				

in a flow-through reactor the output of which is combined with a reagent stream comprising $\text{R1C}_6\text{H}_4\text{CHO}$ in a second flow-through reactor the output of which is received in a reactor containing an acid salt or mineral acid.

RX(1) OF 1



L6 ANSWER 17 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

112:98685 CASREACT

TITLE:

Synthesis and pyrolysis of organoelement benzazole derivatives of phosphorus, arsenic, silicon and tin

AUTHOR(S):

Heinicke, Joachim

CORPORATE SOURCE:

Sekt. Chem., Martin-Luther-Univ., Halle-Wittenberg,
Halle/Saale, 4010, Ger. Dem. Rep.

SOURCE:

Journal of Organometallic Chemistry (1989), 364(3),
C17-C21

DOCUMENT TYPE:

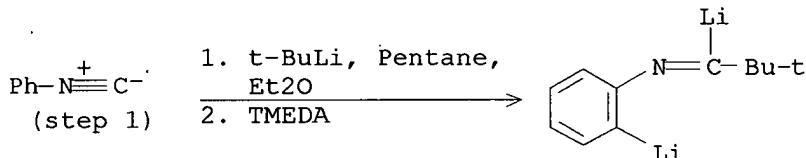
Journal

LANGUAGE:

German

AB 3-Organo-1,3-benzazaphospholes and -benzazasololes as well as 3,3-disubstituted 1,3-benzazasiloles and -benzazastannoles are prepared from $\text{o-LiC}_6\text{H}_6\text{N:C(Li)CMe}_3$ and the relevant organoelement dichlorides. The heterocycles obtained are converted by flash vacuum pyrolysis into the aromatic 1H-1,3-benzazaphospholes and benzazasololes, resp.

RX(1) OF 23



NOTE: thermal

L6 ANSWER 18 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

112:77266 CASREACT

TITLE:

Isolation and crystal structure of a presumed intermediate in the reaction of an organolithium compound with an epoxide

AUTHOR(S):

Harder, Sjoerd; Boersma, Jaap; Brandsma, Lambert;
Kanters, Jan A.; Duisenberg, Albert J. M.; Van Lenthe,
Joop H.

CORPORATE SOURCE:

Dep. Met.-Mediated Synth., Univ. Utrecht, Utrecht,
3584, Neth.

SOURCE:

Organometallics (1990), 9(2), 511-16
CODEN: ORGND7; ISSN: 0276-7333

DOCUMENT TYPE:

Journal

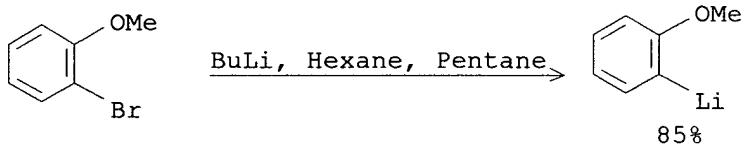
LANGUAGE:

English

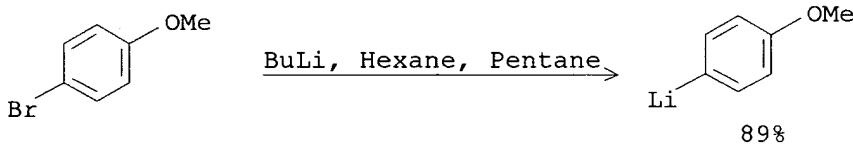
AB The organolithium-epoxide complexes tetrakis(1-lithio-2-methoxybenzene)bis(ethylene oxide) and tetrakis(1-lithio-2-methoxybenzene)bis(propylene oxide), which are thought to be intermediates in the β -hydroxyalkylation of organolithium compds., have been

isolated and characterized. NMR studies on these complexes in nonpolar solvents such as C6H6 and PhMe provide evidence for epoxide O to Li coordination. Addnl., the propylene oxide complex has been characterized by single-crystal x-ray diffraction at 100 K. The structure consists of a tetrameric aggregate of 1-lithio-2-methoxybenzene and two disordered propylene oxide mols., which coordinate to Li as external Lewis bases. Since ab initio calcns. (RHF; SV 3-21G) show the activation of the epoxide by Li coordination to be very small, the question of whether such complexes are intermediates in the nucleophilic ring opening of epoxides remains unanswered.

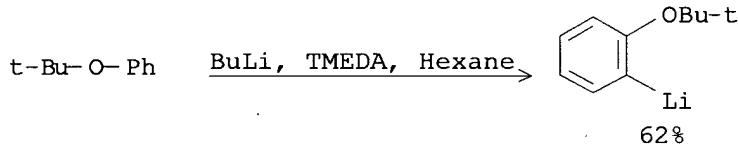
RX(1) OF 7



RX(2) OF 7



RX(3) OF 7



L6 ANSWER 19 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 110:135377 CASREACT

TITLE:

2-Phosphino- and 2-phosphinylbenzenethiols: new ligand types

AUTHOR(S):

Block, Eric; Ofori-Okai, Gabriel; Zubieta, Jon

CORPORATE SOURCE:

Dep. Chem., State Univ. New York, Albany, NY, 12222, USA

SOURCE:

Journal of the American Chemical Society (1989), 111(6), 2327-9

CODEN: JACSAT; ISSN: 0002-7863

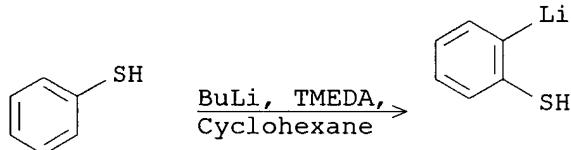
DOCUMENT TYPE: Journal

LANGUAGE: English

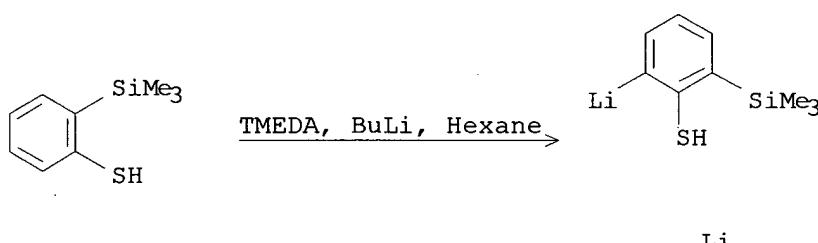
AB Treatment of 2-LiC6H4SLi with Ph2PCl, PhPCl2, PCl3, Ph2P(O)Cl, PhP(O)Cl2, and POCl3 gives, resp., 2-(diphenylphosphino)benzenethiol, bis(2-mercaptophenyl)phenylphosphine, tris(2-mercaptophenyl)phosphine, 2-(diphenylphosphinyl)benzenethiol, bis(2-mercaptophenyl)phenylphosphine oxide (I), and tris(2-mercaptophenyl)phosphine oxide. Treatment of Li 2-lithio-6-trimethylsilylbenzenethiolate with Ph2PCl, PhPCl2, PCl3, Ph2P(O)Cl, PhP(O)Cl2, and POCl3 gives, resp., 2-(diphenylphosphino)-6-trimethylsilylbenzenethiol, bis[2-mercato-6-(trimethylsilyl)phenyl]phenylphosphine, tris[2-mercato-6-(trimethylsilyl)phenyl]phosphine, 2-(diphenylphosphinyl)-6-(trimethylsilyl)benzenethiol, bis[2-mercato-6-(trimethylsilyl)phenyl]phenylphosphine oxide, and tris[2-mercato-6-(trimethylsilyl)phenyl]phosphine oxide. Interesting trends seen in the

³¹P NMR spectra of compds. are discussed. Oxidation of I with DMSO affords 11-phenyl-11H-dibenzo[c,f][1,2,5]dithiaphosphepin 11-oxide, a new heterocyclic ring system. Compds. prepared may be useful as ligands for transition metals.

RX(3) OF 30



RX(4) OF 30



L6 ANSWER 20 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER:

TITLE:
o-Lithiothiophenol equivalents. Generation, reactions
and applications in synthesis of hindered thiolate
ligands

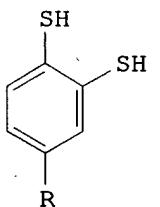
AUTHOR(S):
Block, Eric; Eswarakrishnan, Venkatachalam; Gernon,
Michael; Ofori-Okai, Gabriel; Saha, Chantu; Tang,
Kaluo; Zubietta, Jon

CORPORATE SOURCE:
Dep. Chem., State Univ. New York, Albany, NY, 12222,
USA

SOURCE:
Journal of the American Chemical Society (1989),
111(2), 658-65

DOCUMENT TYPE:
CODEN: JACSAT; ISSN: 0002-7863
Journal
LANGUAGE:
English

GI

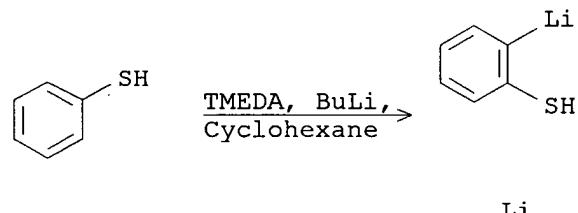


VI

AB Treatment of 2-(phenylthio)tetrahydropyran with Me₃CLi in THF-HMPA at -90° followed by Me₃SiCl or Et₃SiCl and then HgCl₂-H₂S affords 2-(trimethylsilyl)benzenethiol (I) or 2-(triethylsilyl)benzenethiol (II), resp. I and II can also be obtained directly from thiophenol by conversion of the latter to Li 2-lithiobenzenethiolate (III)

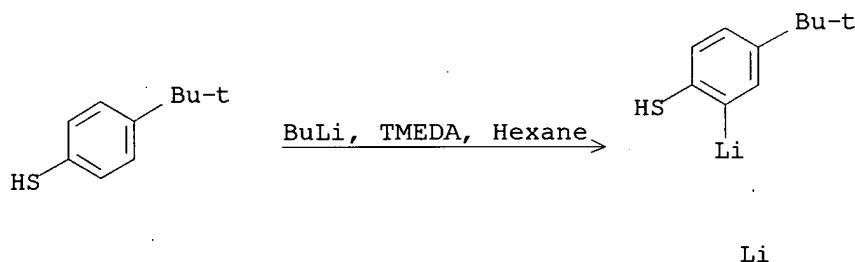
followed by quenching of a THF solution of III at -78° with an equivalent of the appropriate chlorosilane; by this same procedure, 4-tert-butylbenzenethiol can be converted into 4-tert-butyl-2-(trimethylsilyl)benzenethiol via Li 4-tert-butyl-2-lithiobenzenethiolate (IV) and 2-naphthalenethiol can be transformed into 3-(trimethylsilyl)-2-naphthalenethiol via lithium 3-lithio-2-naphthalenethiolate. Reaction of I with BuLi in hexane followed by Me₃SiCl gives 2,6-bis(trimethylsilyl)benzenethiol together with products derived from lithiation of the silyl Me groups. Treatment of III in THF with Me₂SiCl₂ and ClMe₂SiSiMe₂Cl affords bis(2-mercaptophenyl)dimethylsilane (V) and 1,2-bis(2-mercaptophenyl)tetramethyldisilane, resp. Oxidation of V yields 5,5-dimethyldibenzo[b,e]-5-sila-1,2-dithiepin. Treatment of IV with Et₂SiCl₂ and Ph₂SiCl₂ affords bis(4-tert-butyl-2-mercaptophenyl)diethylsilane and bis(4-tert-butyl-2-mercaptophenyl)diphenylsilane, resp. Thiophenol can be transformed into 1,2-benzenedithiol VI (R = H); similarly 4-tert-butylbenzenethiol can be converted into 4-tert-butyl-1,2-benzenedithiol VI (R = Me₃C). Compound VI (R = H) can be further transformed into 1,2,3-benzenetrithiol. The ¹H and ¹³C NMR spectra of dilithio salts III and IV were determined

RX(9) OF 73



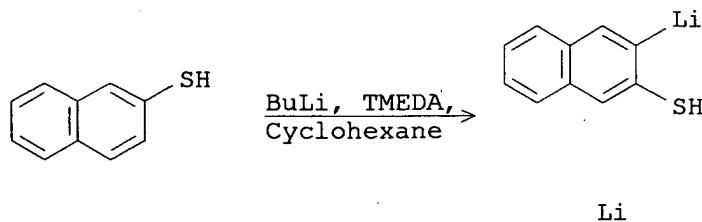
Li

RX(12) OF 73



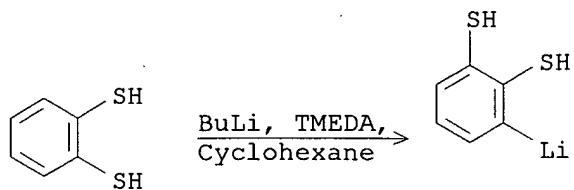
Li

RX(23) OF 73



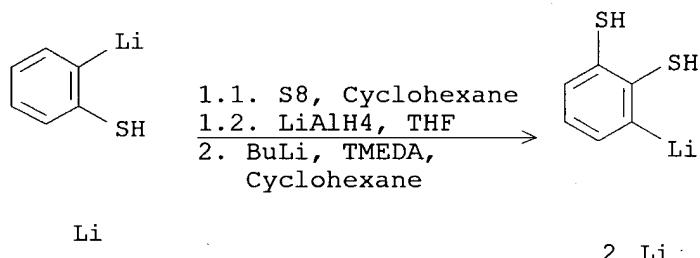
Li

RX(26) OF 73



2 Li

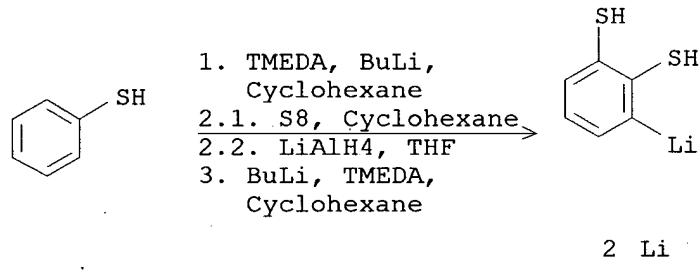
RX(55) OF 73 - 2 STEPS



Li

2 Li

RX(66) OF 73 - 3 STEPS



2 Li

L6 ANSWER 21 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 109:37892 CASREACT

TITLE:

Organophosphorus intermediates. IX. The cleavage of α , ω -bis(diphenylphosphino)alkanes with lithium. A phosphorus-31 NMR study

AUTHOR(S): Brooks, Peter; Gallagher, Michael J.; Sarroff, Adrian
CORPORATE SOURCE: Sch. Chem., Univ. New South Wales, Kensington, 2033, Australia

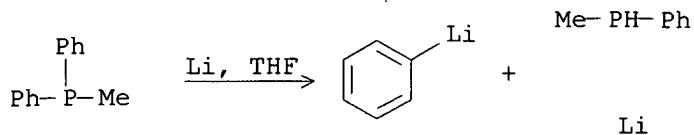
SOURCE: Australian Journal of Chemistry (1987), 40(8), 1341-51
CODEN: AJCHAS; ISSN: 0004-9425

DOCUMENT TYPE: Journal

LANGUAGE: English

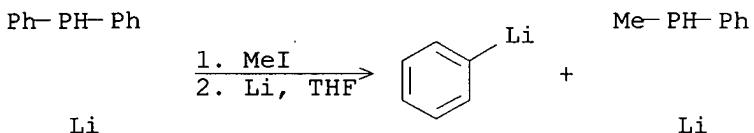
AB The title phosphines, $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ($n = 2-5$), reacts with Li in THF to give the corresponding 1, n -dilithio-1, n -di(phenylphosphines) directly with little or no intermediacy of the 1-lithio-1-phenyl- n -diphenylphosphinoalkanes which can, however, be obtained by arylation of the diphosphides. Methylenebisdiphenylphosphine and 1,4-diphenyl-1,4-diphosphinate undergo exclusive P-alkyl C cleavage. The chemical and ^{31}P NMR spectroscopy of the diphosphides are described and the mechanism of the cleavage reaction is discussed. Some cleavage reactions in liquid ammonia are described.

RX(10) OF 47



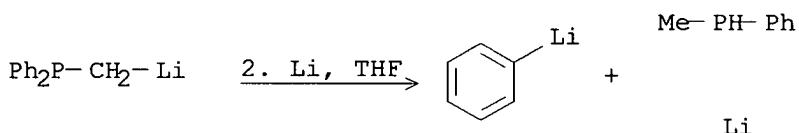
NOTE: Sonication

RX(29) OF 47 - 2 STEPS



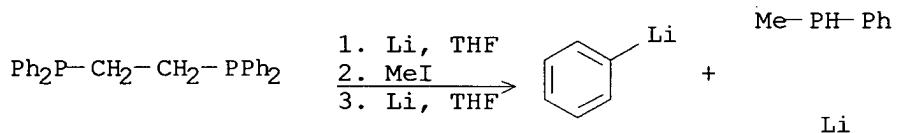
NOTE: 2) Sonication

RX(30) OF 47 - 2 STEPS



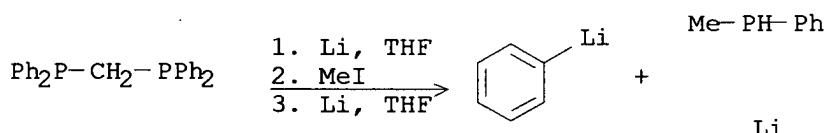
NOTE: 2) Sonication

RX(35) OF 47 - 3 STEPS



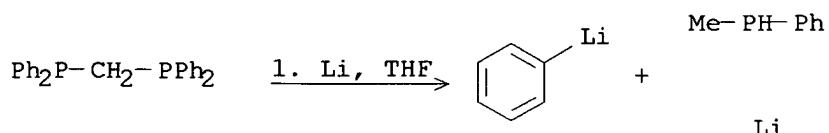
NOTE: 1) Sonication, 3) Sonication

RX(36) OF 47 - 3 STEPS



NOTE: 1) Sonication, 3) Sonication

RX(37) OF 47 - 3 STEPS



NOTE: 1) Sonication, 3) Sonication

L6 ANSWER 22 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 109:23020 CASREACT

TITLE:

Chemistry of organosilicon compounds. 240.
Pentacoordinate allylsilicates: characterization and
highly stereoselective reaction with aldehydes

AUTHOR(S):

Kira, Mitsuo; Sato, Kazuhiko; Sakurai, Hideki

CORPORATE SOURCE:

Fac. Sci., Tohoku Univ., Sendai, 980, Japan

SOURCE:

Journal of the American Chemical Society (1988),
110(14), 4599-602

CODEN: JACSAT; ISSN: 0002-7863

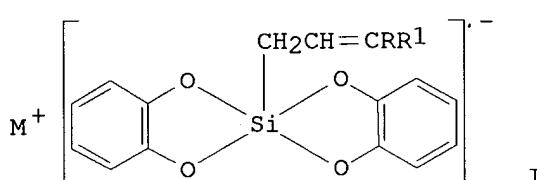
DOCUMENT TYPE:

Journal

LANGUAGE:

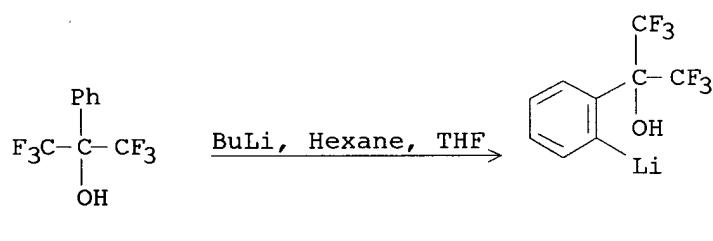
English

GI



AB Lithium and bis(triphenylphosphoranylidene)ammonium salts of bis(1,2-benzenediolato)allylsilicates, i.e., I [R, R1 = H, Me; M = Li, (Ph3P)2N] which were prepared by reaction of allyl-, phenyl-, and (E)- and (Z)-crotyltrichlorosilanes with dilithium catecholate, reacted with PhCHO or furfural to give the corresponding homoallyl alcs. in a regiospecific and highly diastereoselective manner in 80-90% yields. A six-membered cyclic transition state, which is favored by the enhanced nucleophilicity of the γ -carbon of the allylsilicates as well as by the significant Lewis acidity giving hexacoordinate silicates, is proposed. However, allylsilicates with α,α -bis(trifluoromethyl)benzenemethanolato(2-)C2,O ligands did not react with the aldehydes.

RX(17) OF 50



Li

L6 ANSWER 23 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 108:131983 CASREACT

TITLE:

Reactions of MC15 (M = niobium or tantalum) with excess phenyllithium: structural characterization of bisbenzyne/polyphenyl derivatives of niobium and tantalum

AUTHOR(S):

Bartlett, Ruth A.; Power, Philip P.; Shoner, Steven C.

CORPORATE SOURCE:

Dep. Chem., Univ. California, Davis, CA, 95616, USA

SOURCE:

Journal of the American Chemical Society (1988),

110(6), 1966-8
CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE:

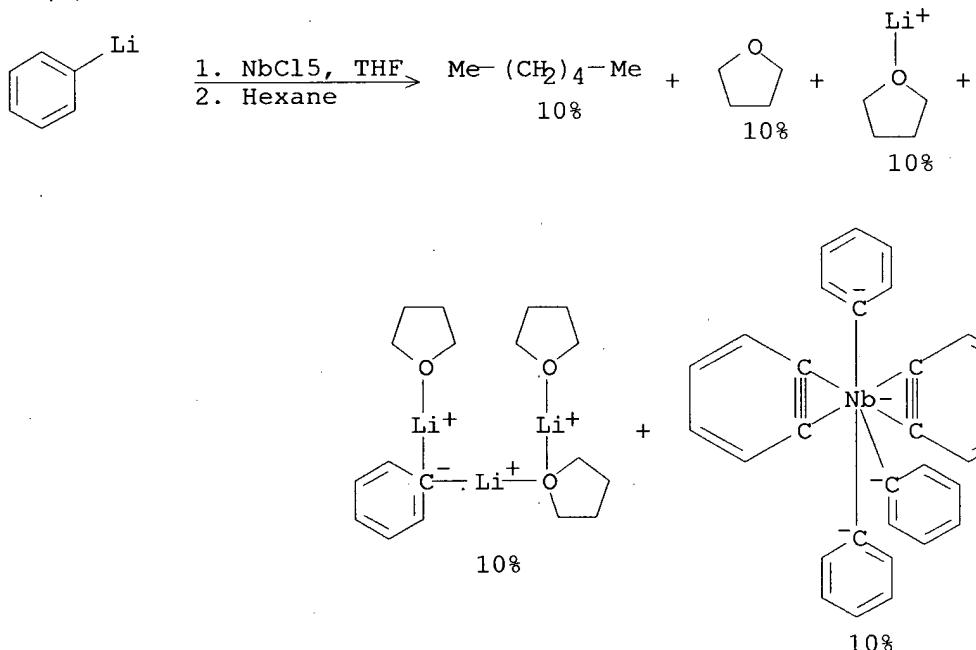
Journal

LANGUAGE:

English

AB The complexes $[\text{Nb}(\eta^2\text{-C}_6\text{H}_4)\text{2Ph}_3(\text{LiPh}\cdot\text{THF})(\text{LiTHF})_4]\cdot0.5$ $\text{THF}\cdot0.5\text{ n-C}_6\text{H}_14$ (I) and $[\text{Ta}(\eta^2\text{-C}_6\text{H}_4)\text{2Ph}_4(\text{LiTHF})_2]_2[\text{Li}_4\text{Cl}_2(\text{THF})_1$ 0] were prepared from MC_15 ($\text{M} = \text{Nb, Ta}$) and PhLi . They are the first examples of mononuclear bisbenzyne derivs. and appear to be stabilized by inclusion of several solvated Li^+ ions. In I $\text{Nb}(\text{III})$ is surrounded in a roughly trigonal bipyramidal fashion by 3 Ph and 2 benzyne groups with 5 associated THF-solvated Li^+ ions and another Ph group. $\text{Ta}(\text{V})$ complex II has a distorted octahedral coordination of 4 Ph groups and 2 cis-benzynes with 2 associated solvated Li^+ ions. Longer C-C distances involving the benzyne ligands suggest that the transition metal centers are fairly electron-rich.

RX(1) OF 2



L6 ANSWER 24 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 108:131538 CASREACT

TITLE: Tandem arylation-reduction of acyl heterocycles.

Convenient synthesis of benzyl heterocycles

Hall, Stan S.; Farahat, Sami E.

AUTHOR(S):
CORPORATE SOURCE: Dep. Chem., Rutgers, State Univ., Newark, NJ, 07102,
USA

SOURCE: Journal of Heterocyclic Chemistry (1987), 24(4),
1205-13

CODEN: JHTCAD; ISSN: 0022-152X

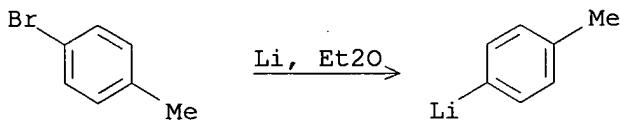
DOCUMENT TYPE: Journal

LANGUAGE: English

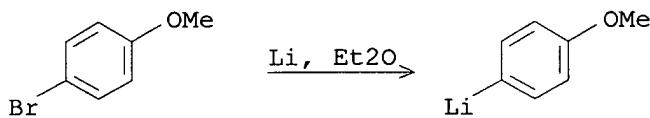
AB Tandem arylation-reduction of a series of acyl heterocycles using $4\text{-RC}_6\text{H}_4\text{Li}$ ($\text{R} = \text{H, Me, MeO}$), followed by $\text{Li}/\text{NH}_3/\text{NH}_4\text{Cl}$ reduction afforded the corresponding benzyl heterocycles in 38-99% yields. The acyl heterocycles surveyed in this study contained furan, 2,3-dihydro-4H-1-benzopyran, 4H-1-benzopyran, thiophene, 4,5,6,7-tetrahydrobenzo[b]thiophene, 2,3-dihydro-4H-1-benzothiopyran, and pyridine nuclei. All acyl heterocycles yielded the corresponding benzyl heterocycles except

2,3-dihydro-4H-1-benzothiopyran-4-one, which selectively cleaved during reduction to give the corresponding 2-(1-arylpropyl)benzenethiols.

RX(40) OF 81



RX(41) OF 81



L6 ANSWER 25 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 108:94687 CASREACT

TITLE:

Tetraphenylcyclopentadiene and (4-tert-butylphenyl)tetraphenylcyclopentadiene: synthesis and characterization of their alkali-metal salts and metallocenes of germanium, tin, and lead

AUTHOR(S):

Schumann, Herbert; Janiak, Christoph; Zuckerman, Jerold J.

CORPORATE SOURCE:

Inst. Anorg. Anal. Chem., Tech. Univ. Berlin, Berlin, D-1000/12, Fed. Rep. Ger.

SOURCE:

Chemische Berichte (1988), 121(2), 207-18

CODEN: CHBEAM; ISSN: 0009-2940

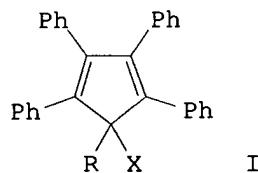
DOCUMENT TYPE:

Journal

LANGUAGE:

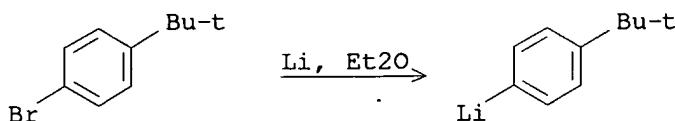
German

GI

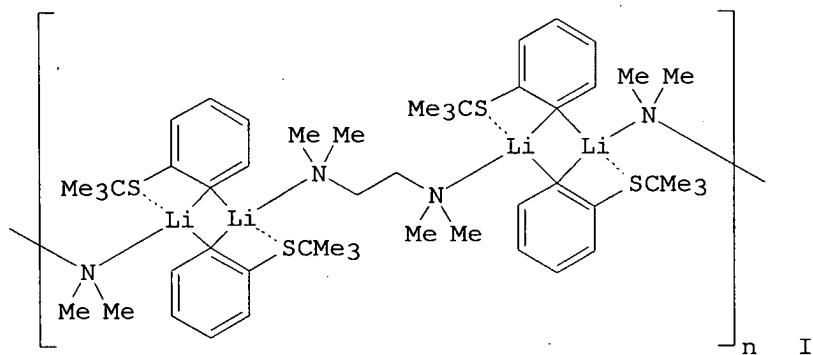


AB Title compds. I (R = H, Ph, 4-Me₃CC₆H₄; X = H, Li, Na, K, Br, OH) and the Ge, Sn, and Pb metallocenes of I (R = H, 4-Me₃CC₆H₄; X = H) were prepared IR, Raman, ¹H and ¹³C NMR and mass spectral data and x-ray powder diagrams were reported. Comparative ¹³C NMR studies showed delocalization of the neg. charge from the cyclopentadiene ring into the nonparallel Ph ligands.

RX(22) OF 185

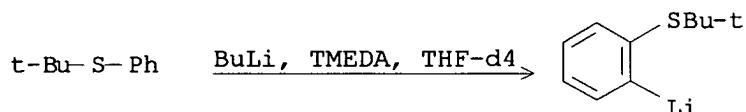


L6 ANSWER 26 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 108:75448 CASREACT
 TITLE: Structure of 2-lithiophenyl tert-butyl thioether in solution and in the solid state. Detection of agostic lithium-hydrogen interactions by NMR spectroscopy
 AUTHOR(S): Bauer, Walter; Klusener, P. A. A.; Harder, Sjoerd; Kanters, J. A.; Duisenberg, A. J. M.; Brandsma, Lambert; Schleyer, Paul v. R.
 CORPORATE SOURCE: Org. Chem. Lab., Rijksuniv. Utrecht, 3584 CH, Neth.
 SOURCE: Organometallics (1988), 7(2), 552-5
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 GI



AB Tert-Bu phenyl thioether, in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA), is deprotonated with BuLi in hexane to give the ortho lithiation product I. X-ray anal. shows I to be an endless polymer with dimeric centrosym. subunits linked by TMEDA acting as a bridging ligand. The lithiated C atom tends toward planar tetracoordination. However, a different structure is present in solution Structural assignments for I in THF solution are made by one- and two-dimensional NMR spectroscopy. Complete dissociation into monomers is indicated by ¹³C NMR (signal multiplicities and ¹³C, ⁶Li coupling consts.). Close Li-H contacts (detected by ⁶Li-¹H 2D heteronuclear Overhauser spectroscopy, HOESY) are observed for the aromatic H atom vicinal to the Li substituent and for the Me3C group. However, TMEDA apparently is not bound to Li in THF solution

RX(2) OF 2



L6 ANSWER 27 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 108:21630 CASREACT
 TITLE: Regioselective generation and trapping of mono- and dianions of 3-(arylsulfonyl)furans. Bidentate carbanion stabilization via sulfones
 AUTHOR(S): Hartman, George D.; Halczenko, Wasyl
 CORPORATE SOURCE: Merck Sharp and Dohme Res. Lab., West Point, PA,

SOURCE:

19486, USA

Tetrahedron Letters (1987), 28(28), 3241-4

CODEN: TELEAY; ISSN: 0040-4039

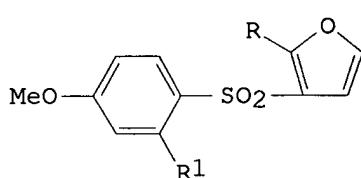
DOCUMENT TYPE:

Journal

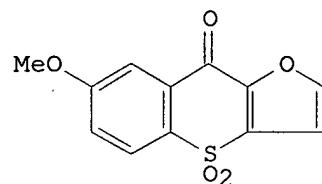
LANGUAGE:

English

GI



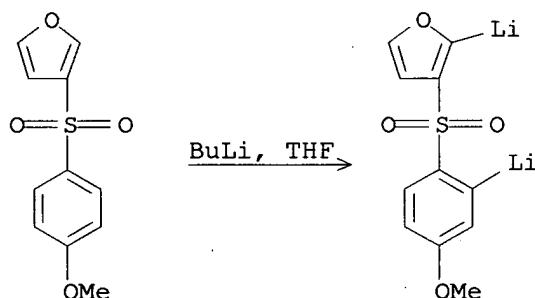
I



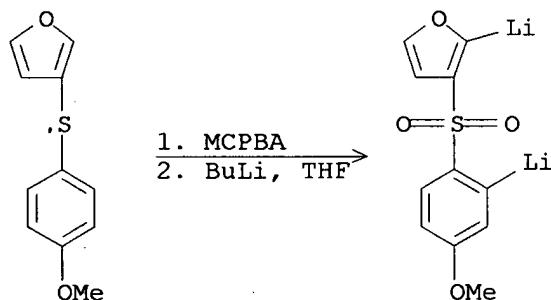
IV

AB Lithiation of methoxyphenylsulfonylfuran I (R = R1 = H) with 1 equivalent BuLi gave lithio derivative I (R = Li, R1 = H), which was trapped with D2O or Me2N+CH2 I- (II) to give adducts I (R = D, CH2NMe2, R1 = H). Lithiation of I (R = R1 = H) with 2 equivalent BuLi regiospecifically gave dilithio derivative I (R = R1 = Li) (III). III was trapped with excess D2O or II to give disubstituted adducts I (R = R1 = D, CH2NMe2), with 1 equivalent II to give I (R = H, R1 = CH2NMe2), and with (EtO)2CO to give tricyclic ketone IV.

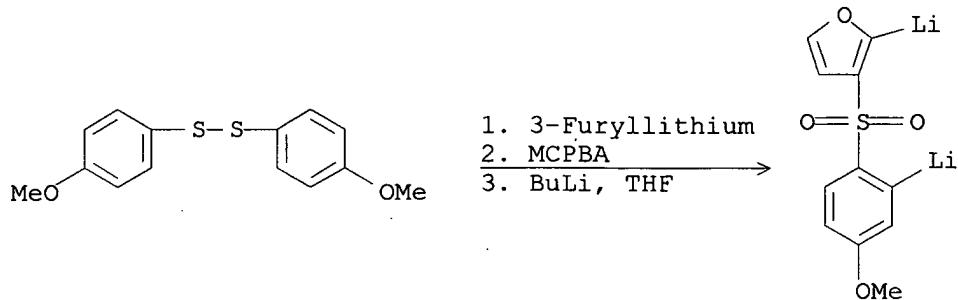
RX(5) OF 33



RX(12) OF 33 - 2 STEPS



RX(33) OF 33 - 3 STEPS



L6 ANSWER 28 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 107:7241 CASREACT

TITLE: Lithium and sodium derivatives of N-substituted 2-alkylbenzimidazoles

AUTHOR(S): Tertov, B. A.; Bogachev, Yu. G.; Koshchienko, Yu. V.; Suvorova, G. M.; Tsupak, E. B.; Chub, N. K.; Breus, S. F.

CORPORATE SOURCE: Rostov. Gos. Univ., Rostov, USSR

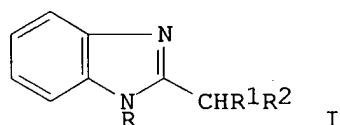
SOURCE: Khimiya Geterotsiklicheskikh Soedinenii (1986), (8), 1073-7

CODEN: KGSSAQ; ISSN: 0453-8234

DOCUMENT TYPE: Journal

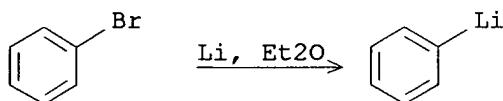
LANGUAGE: Russian

GI



AB The title compds. (I; R = Me, Ph; R1 = H, Me, Et, R2 = Li, Na) were prepared in 90-6% yields by metalation of I (R1 = H) with R3Li or R3Na (R3 = Bu, Ph, naphthyl). The preparation of other derivs. by treating I (R2 = Li, Na) with Ph2CO, PrONO2, aldehydes, and iodides was also discussed. Thus, treating I (R = Me, R1 = H, R2 = Na) with MeI gave the corresponding I (R2 = Me).

RX(38) OF 82



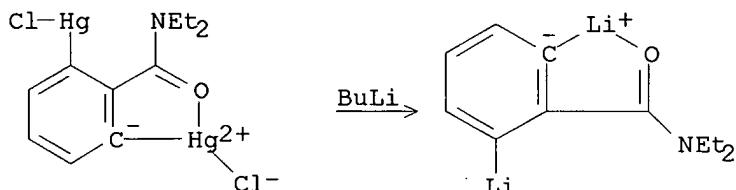
L6 ANSWER 29 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 106:119913 CASREACT

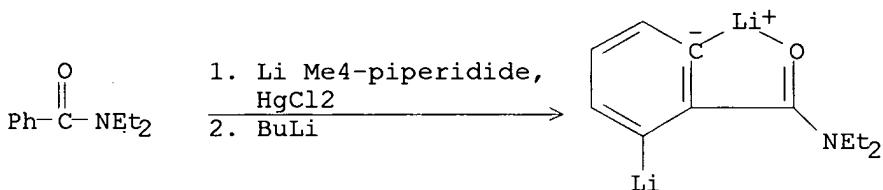
TITLE: Reverse transmetalation: a strategy for obtaining certain otherwise difficultly accessible

AUTHOR(S): organometallics
 Eaton, Philip E.; Cunkle, Glen T.; Marchioro, Gaetano;
 Martin, Ronald M.
 CORPORATE SOURCE: Dep. Chem., Univ. Chicago, Chicago, IL, 60637, USA
 SOURCE: Journal of the American Chemical Society (1987),
 109(3), 948-9
 CODEN: JACSAT; ISSN: 0002-7863
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB Li and Grignard derivs. of amide activated cubanes are made in high yield and free of interfering reactants by treatment of the corresponding cubylmercury with CH₃Li or CH₃MgBr. As the cubylmercury is obtained by transmetalation trapping of a small equilibrium concentration of the cubyllithium, the process is called reverse transmetalation. Similar organometallics are available using these processes on an amide activated cyclopropane. Double reverse transmetalation is used for the preparation of dilithio and di-Grignard derivs. of a cubane diamide.

RX(1) OF 16



RX(15) OF 16 - 2 STEPS



L6 ANSWER 30 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 106:33276 CASREACT

TITLE: Binding of platinum(II) via a σ-Pt-C bond to a novel type of macrocyclic monoanionic carbodiaza ligand: x-ray crystal structure of trans[2,6-(2,13-dimethyl-2,13-diazatetradecanediyl)phenyl-N,N']platinum(II) iodide
 AUTHOR(S): Terheijden, Jos; Van Koten, Gerard; Van Beek, Johannus A. M.; Vriesema, Bindert K.; Kellogg, Richard M.; Zoutberg, Martin C.; Stam, Casper H.
 CORPORATE SOURCE: Anorg. Chem. Lab., Univ. Amsterdam, Amsterdam, 1018 WV, Neth.

SOURCE: Organometallics (1987), 6(1), 89-93
 CODEN: ORGND7; ISSN: 0276-7333

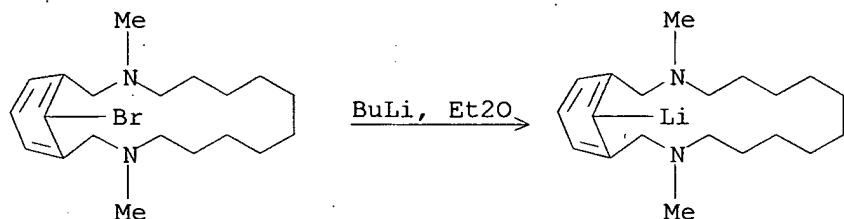
DOCUMENT TYPE: Journal
 LANGUAGE: English

GI For diagram(s), see printed CA Issue.

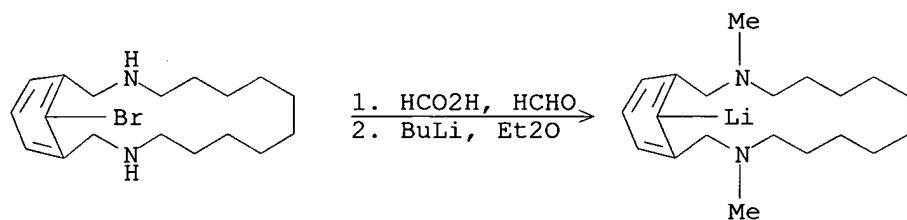
AB The macrocyclic, monoanionic carbodiaza ligand 3,14-diaza-20-bromo-3,14-dimethylbicyclo[14.3.1]eicosa-1(20),16,18-triene (I) was prepared in 55% yield from 2,6-(BrCH₂)₂C₆H₃Br and p-MeC₆H₄SO₂NH(CH₂)₁₀NHSO₂C₆H₄Me-p in the presence of Cs₂CO₃. Detosylation with HBr and methylation with HCHO-HCO₂H afforded I. The organoplatinum complex II is the 1st example of an

organometallic cage compound. Its preparation involved reaction of $[\text{PtCl}_2(\text{SEt}_2)_2]$ with the Li derivative of I, followed by halide exchange with NaI in Me_2CO . II contains a divalent Pt center with the N donor atoms positioned trans owing to the geometric constraints of the terdentate coordination. Single-crystal x-ray diffraction established the structure of II as having a long hydrocarbon chain bending away from the coordination plane.

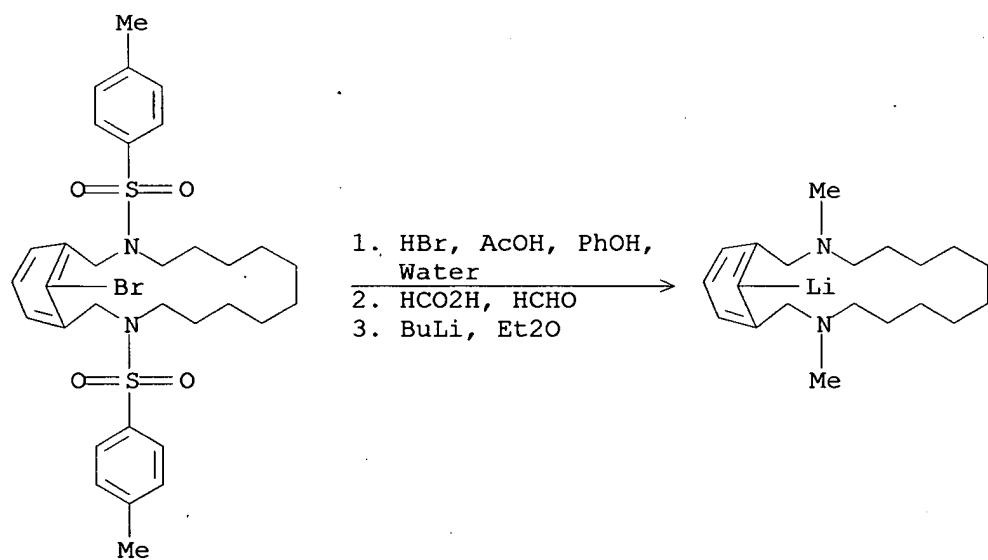
RX(4) OF 15



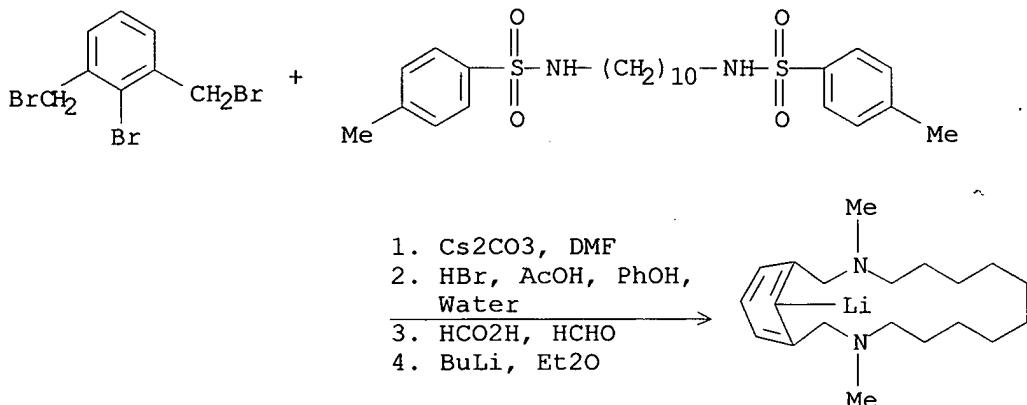
RX(8) OF 15 - 2 STEPS



RX(11) OF 15 - 3 STEPS

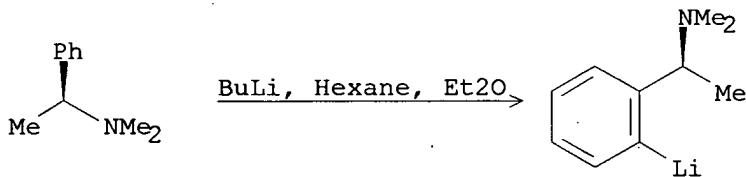


RX(12) OF 15 - 4 STEPS



L6 ANSWER 31 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 106:32467 CASREACT
TITLE: Steric consequence of the diastereoselective addition
of chiral lithium 2-(1-dimethylaminoethyl)phenyl
cuprates to some enones
AUTHOR(S): Andersson, Staffan; Jagner, Susan; Nilsson, Martin;
Urso, Fabio
CORPORATE SOURCE: Dep. Inorg. Chem., Chalmers Univ. Technol., Goeteborg,
S-412 96, Swed.
SOURCE: Journal of Organometallic Chemistry (1986), 301(2),
257-67
CODEN: JORCAI; ISSN: 0022-328X
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Conjugate addition of the chiral Li [(S)-2-(1-dimethylaminoethyl)phenyl](2-thienyl)cuprate to (E)-4-phenyl-3-buten-2-one, 2-cyclohexenone or 2-cyclopentenone gave with high diastereoselectivity (S,S)-4-[2-(1-dimethylaminoethyl)phenyl]-4-phenyl-2-butenone, (S,S)-3-[2-(1-dimethylaminoethyl)phenyl]-2-cyclohexanone, and (S,S)-1-[3-oxocyclopentyl]phenyl]ethyltrimethylammonium iodide. The (S,S)-configuration observed in the adducts indicated that the conjugate addition gave the least crowded Li enolate as the major product.

RX(1) OF 16



L6 ANSWER 32 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 105:208987 CASREACT
TITLE: New methods for the synthesis of proximally
functionalized arylboranes and silanes
AUTHOR(S): Katz, H. E.
CORPORATE SOURCE: AT and T Bell Lab., Murray Hill, NJ, 07974, USA
SOURCE: Organometallics (1986), 5(11), 2308-11
CODEN: ORGND7; ISSN: 0276-7333

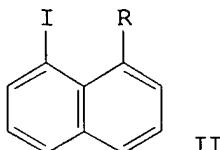
DOCUMENT TYPE:

Journal

LANGUAGE:

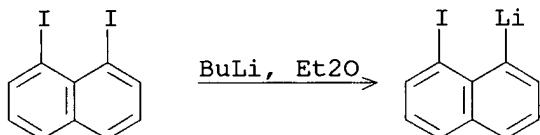
English

GI



AB The synthesis of ten novel disubstituted aromatic compds. is reported. New methods that were developed for the syntheses include (1) single I-Li exchange of 1,8-diiodonaphthalene, (2) use of Me₃SiOSO₂CF₃ (I) to form C-Si bonds in sterically hindered situations, and (3) protection of an organoborane as an ethoxy ate complex during halogen-metal exchange and substitution on the organic residue. In addition, the dimethylborylation of aryllithium reagents with Me₂BOEt was generalized to include labile nucleophiles. The methods are geared to the synthesis of perisubstituted naphthalenes as anion receptors but should be of more general utility as well. Finally, some special properties of the newly synthesized compds. are discussed. E.g., the reaction of iodonaphthalene derivative II (R = Li) with I, B(OEt)₃, and EtOBMe₂ gave 65-83% I [R = SiMe₃, B(OEt)₂, BMe₂], resp.

RX(1) OF 28



L6 ANSWER 33 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

105:24745 CASREACT

TITLE:

Quaternized cyclic and high polymeric phosphazenes and their interactions with tetracyanoquinodimethane

AUTHOR(S):

Allcock, Harry R.; Levin, Michael L.; Austin, Paul E.

CORPORATE SOURCE:

Dep. Chem., Pennsylvania State Univ., University Park, PA, 16802, USA

SOURCE:

Inorganic Chemistry (1986), 25(14), 2281-8

CODEN: INOCAJ; ISSN: 0020-1669

DOCUMENT TYPE:

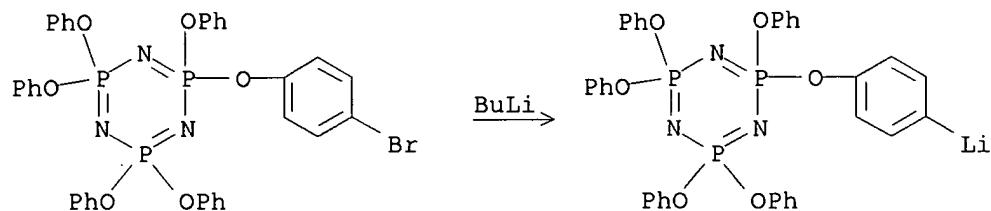
Journal

LANGUAGE:

English

AB Small-mol. cyclotri- or cyclotetraphosphazenes and their linear high polymeric analogs bearing amino, phosphino, or organohalo side groups were quaternized by treatment with MeI or Ph₃P. Quaternization occurred at the side-group sites except with the piperidino derivs., where the reactive sites were the skeletal nitrogen atoms. The quaternized species reacted with Li 7,7,8,8-tetracyanoquinodimethane [1283-90-5] to generate TCNQ "simple salts", and these (or their onium precursors) reacted with neutral TCNQ to generate the "complex salts". The elec. conductivities of the cyclic trimeric phosphazene complex salts (10⁻³-10⁻² Ω⁻¹ cm⁻¹) were higher than those of their high polymeric counterparts.

RX(5) OF 24



L6 ANSWER 34 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

104:68510 CASREACT

TITLE:

Dianion metalation reactions of N,N-dimethylvanillylamine and N,N-dimethylisovanillylamine

AUTHOR(S):

Hlasta, Dennis J.; Bell, Malcolm R.

CORPORATE SOURCE:

Sterling-Winthrop Res. Inst., Rensselaer, NY, 12144, USA

SOURCE:

Tetrahedron Letters (1985), 26(18), 2151-4

CODEN: TELEAY; ISSN: 0040-4039

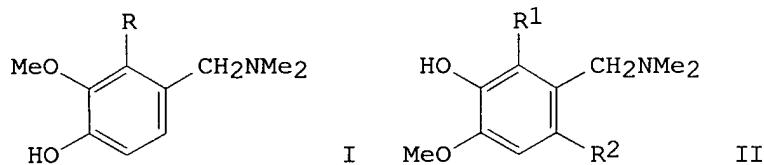
DOCUMENT TYPE:

Journal

LANGUAGE:

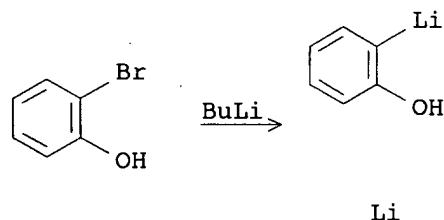
English

GI



AB The utility of dianion chemical in the synthesis of polyfunctional aroms. is demonstrated by the direct lithiation of the vanillylamine I (R = H) and by the Li-Br exchange reaction of isovanillylamines II (R1 = H, R2 = Br; R1 = Br, R2 = H). Condensation of the lithiated dianions with Ph2CO and 4-PhCH2OC6H4CHO yielded I [R = CPh2OH, CH(OH)C6H4OCH2Ph-4] and II (R1 = H, R2 = CPh2OH; R1 = CPh2OH, R2 = H). Lithiation and subsequent reaction with D2O yielded no detectable dianion formation for II (R1, R2 = H), 2-HOC6H4OMe, and 4-HOC6H4CH2NMe2.

RX(4) OF 6



L6 ANSWER 35 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 104:34182 CASREACT

TITLE:

Syntheses of cis- and trans-bis(substituted

phenyl)bis(tributylphosphine)platinum(II) compounds with substituents of π -acceptor character in the platinum-bound phenyl rings

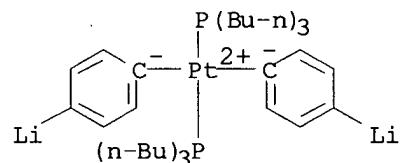
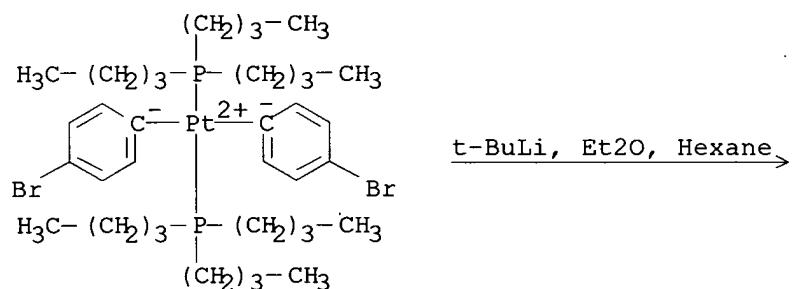
AUTHOR(S): Mueller, Wolf Dieter; Brune, Hans Albert
CORPORATE SOURCE: Abt. Theor. Chem., Univ. Ulm, Ulm/Donau, D-7900, Fed. Rep. Ger.

SOURCE: Chemische Berichte (1985), 118(11), 4347-55
CODEN: CHBEAM; ISSN: 0009-2940

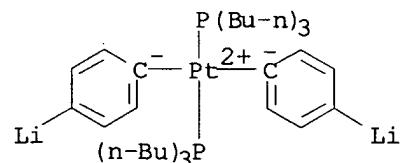
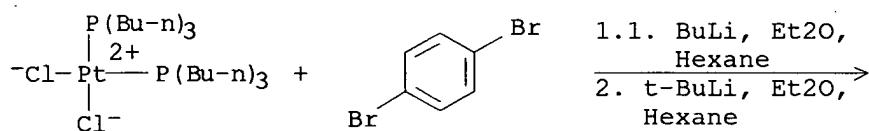
DOCUMENT TYPE: Journal
LANGUAGE: German

AB cis -[Pt(PBu₃)₂(C₆H₄R-p)₂] (cis -I; R = D, SiMe₃, CO₂H, CO₂Me, cyano, COPh) and $trans$ -I (R = iodo) were prepared by treating cis -I (R = Li) with suitable reagents. cis -I were converted to $trans$ -I by catalysis with Bu₄N⁺ I⁻.

RX(15) OF 48



RX(23) OF 48 - 2 STEPS



L6 ANSWER 36 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 102:166432 CASREACT
TITLE: Possibilities and limits of the anionically induced

sulfonamide-amino sulfone rearrangement

AUTHOR(S): Hellwinkel, Dieter; Lenz, Ruediger
CORPORATE SOURCE: Org.-Chem. Inst., Univ. Heidelberg, Heidelberg, D-6900/1, Fed. Rep. Ger.

SOURCE:

Chemische Berichte (1985), 118(1), 66-85

CODEN: CHBEAM; ISSN: 0009-2940

DOCUMENT TYPE:

Journal

LANGUAGE:

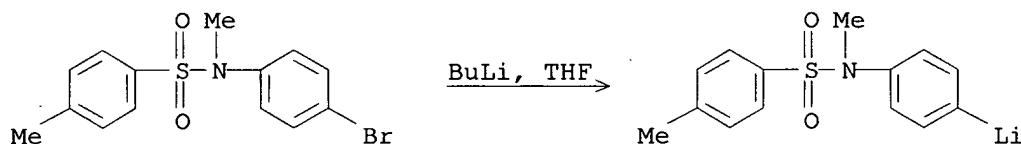
German

GI

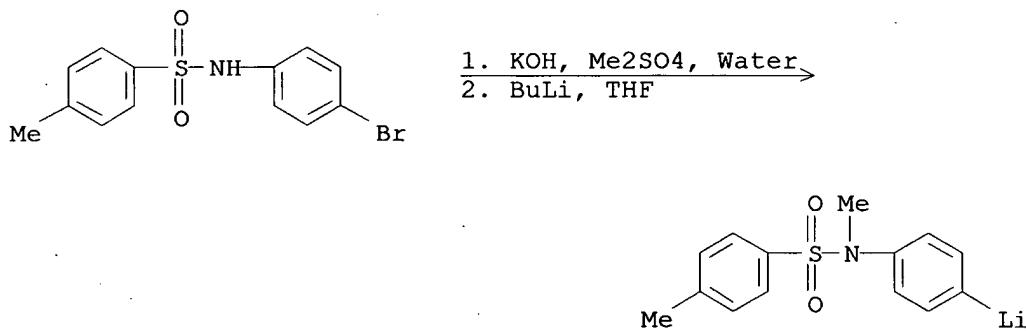
* STRUCTURE DIAGRAM TOO LARGE FOR DISPLAY - AVAILABLE VIA OFFLINE PRINT *

AB When applying the title reaction to naphthyltoluenesulfonamides I (N at 1, 2), the [1,3] shift of the arylsulfonyl group proceeds to the 3- and 2-position, to give II and III (R = H), resp., which is in full compliance with optimal conjugative and steric conditions for the relevant intermediates II and III (R = Li). Attempts to initiate comparable [1,5] rearrangements via the o-lithiated biphenyl derivative IV and p-lithiated 4-LiC₆H₄NMeSO₂C₆H₄Me-4 gave, after extended transmetalation cascades, conventional [1,3] rearrangement products V and 2-MeNHC₆H₄SO₂C₆H₄Me-4, resp. While attempting to cause an anionically-induced [1,4] sulfonyl shift in 2-MeC₆H₄NMeSO₂Ph (VI) into the benzyl position, 2 fragments of VI combined to give the novel heteropolycycle VII. Contrary to the literature, sulfonamides VIII (R₁ = H, Me) also rearranged photolytically to o-amino sulfones IX.

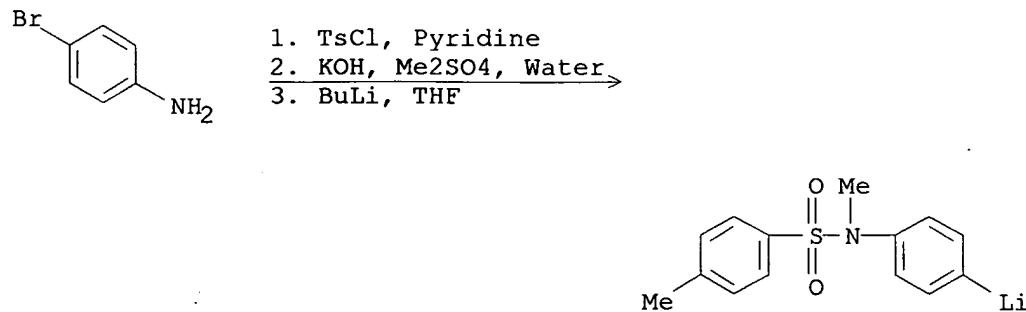
RX(19) OF 86



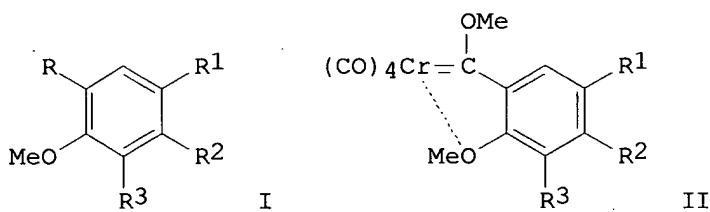
RX(51) OF 86 - 2 STEPS



RX(74) OF 86 - 3 STEPS

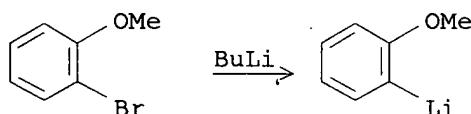


L6 ANSWER 37 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 102:113657 CASREACT
TITLE: Carbene ligands as anthracyclinone synthons. I.
AUTHOR(S): Methoxyarylcarbene as chelating ligands
Doetz, Karl Heinz; Sturm, Werner; Popall, Michael;
Riede, Juergen
CORPORATE SOURCE: Anorg. Chem. Inst., Tech. Univ. Muenchen, Garching,
D-8046, Fed. Rep. Ger.
SOURCE: Journal of Organometallic Chemistry (1984), 277(2),
267-75
DOCUMENT TYPE: CODEN: JORCAI; ISSN: 0022-328X
LANGUAGE: Journal
GI German

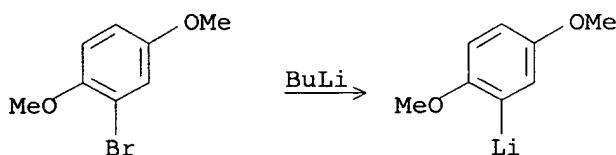


AB Pentacarbonyl[methoxy(1-methoxy-2-aryl)carbene]chromium complexes I [R = C(OMe):Cr(CO)5; R1 = H, OMe, R2 = R3 = H, R2R3 = CH:CHCH:CH; R1 = R3 = H, R2 = OMe] are obtained via successive addition of I (R = Li) and Me3O+BF4- to Cr(CO)6. I [R = C(OMe):Cr(CO)5] undergo intramol. CO-substitution to give cis-tetracarbonyl[methoxy(1-methoxy-2-aryl)carbene] complexes II. Coplanarity of the "chromabenzofuran" system was established by x-ray anal. of II (R1-R3 = H). II analogs have been used as synthons for anthracyclinones.

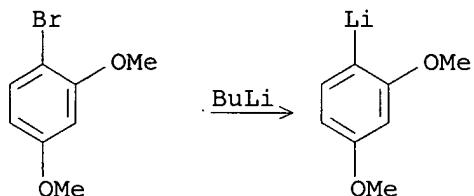
RX(1) OF 4



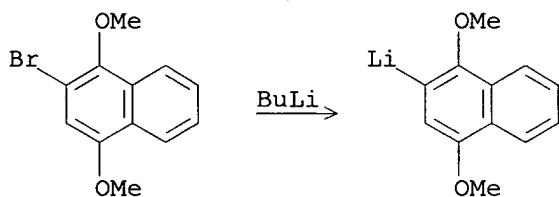
RX (2) OF 4



RX(3) OF 4



RX(4) OF 4



L6 ANSWER 38 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 101:90538 CASREACT

TITLE: Preparation and lithiation of optically active 2,2'-dihalo-1,1'-binaphthyls. A general strategy for obtaining chiral, bidentate ligands for use in asymmetric synthesis

AUTHOR(S): Brown, Kenneth J.; Berry, Matthew S.; Waterman, Kenneth C.; Lingenfelter, David; Murdoch, Joseph R.

CORPORATE SOURCE: Dep. Chem. Biochem., Univ. California, Los Angeles, CA, 90024, USA

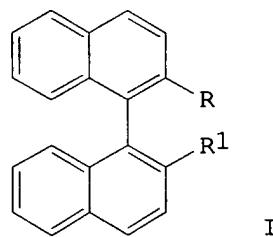
SOURCE: Journal of the American Chemical Society (1984), 106(17), 4717-23

CODEN: JACSAT; ISSN: 0002-7863

DOCUMENT TYPE: Journal

LANGUAGE: English

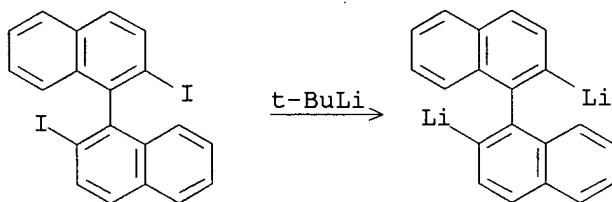
GI



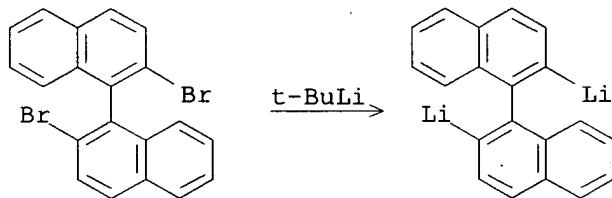
AB Binaphthyls I (R = R¹ = Br, iodo) of up to 98% optical purity were mono- or dilithiated to give I (R = Li, R¹ = Li, Br, iodo), which were configurationally stable from -131 to up to at least -44°. (R)-I (R = R¹ = iodo) with 43.7 ± 1, 48.1 ± 2, and >98% ee (ee = enantiomeric excess) reacted with PhCHO to give 42.7 ± 3, 47.2 ± 3, and >98% ee, resp., (R)-I (R = HOCHPh, R¹ = H). (R)- And (S)-I (R = R¹ = iodo) with 88.5 ± 5 and 57.7 ± 3% ee, resp., gave

(R)- and (S)-I ($R = R_1 = PPh_2$) with 86.5 ± 1 and $57.2 \pm 1\%$ ee upon treatment with $ClPPh_2$.

RX(2) OF 4



RX(3) OF 4



L6 ANSWER 39 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 100:6594 CASREACT

TITLE:

Regioselective metalation of aromatic compounds. II. Second metalation and 1-lithionaphthalene and 9-lithioanthracene.

AUTHOR(S):

Neugebauer, Wolfgang; Clark, Timothy; Schleyer, Paul v. R.

CORPORATE SOURCE:

Inst. Org. Chem., Univ. Erlangen-Nurnberg, Erlangen, D-8520, Fed. Rep. Ger.

SOURCE:

Chemische Berichte (1983), 116(10), 3283-92

CODEN: CHBEAM; ISSN: 0009-2940

DOCUMENT TYPE:

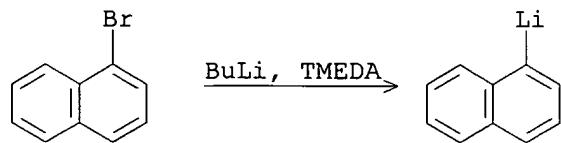
Journal

LANGUAGE:

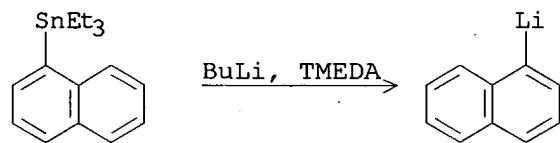
German

AB Both 1-lithionaphthalene and 9-lithioanthracene undergo specific metalations whereby a second Li is introduced at the adjacent peri-positions in the presence of $BuLi\text{-}Me_2NCH_2CH_2NMe_2$. Explanations for such directed second metalations, for which other examples are known, are provided by MNDO calcns. The dilithiated products are stabilized by sym. double bridging. The LUMO coeffs. on the activated H in the monolithio precursors are largest and the C-H bond lengths longest. Dimers, more realistic models for the solution species, show these characteristics as well.

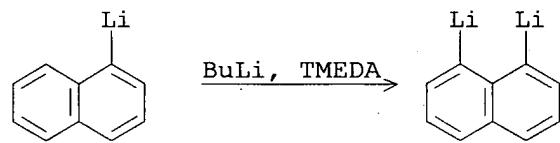
RX(10) OF 51



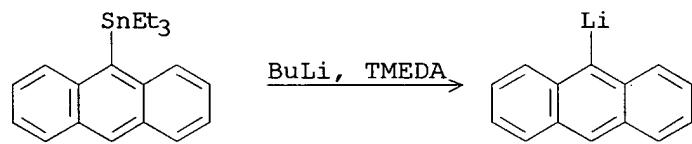
RX(11) OF 51



RX(12) OF 51



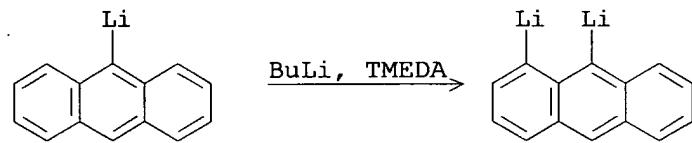
RX(14) OF 51



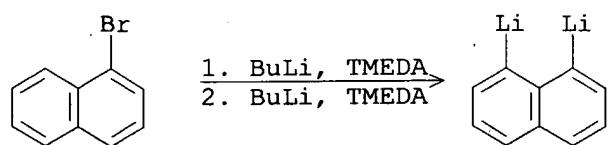
RX(15) OF 51



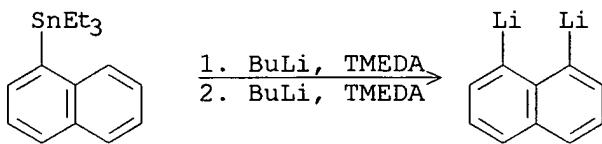
RX(16) OF 51



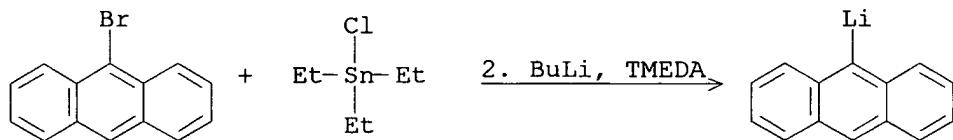
RX(21) OF 51 - 2 STEPS



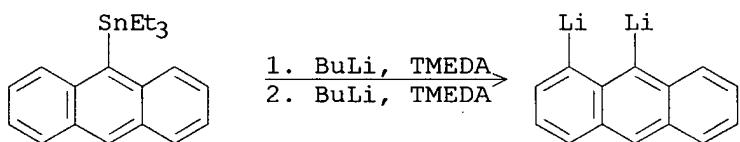
RX(24) OF 51 - 2 STEPS



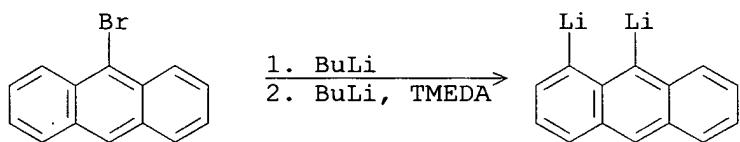
RX(27) OF 51 - 2 STEPS



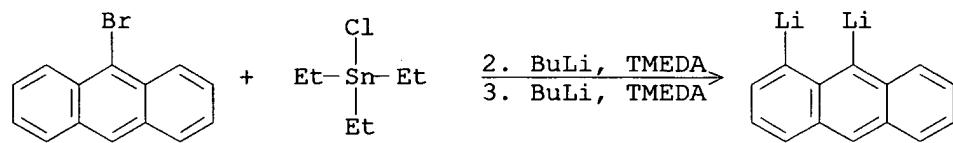
RX(30) OF 51 - 2 STEPS



RX(33) OF 51 - 2 STEPS



RX(45) OF 51 - 3 STEPS



L6 ANSWER 40 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 99:175902 CASREACT

TITLE:

Reactions' of lithium o-lithiophenolate and lithium o-lithio-N-methylanilide with halides of phosphorus, arsenic and silicon

AUTHOR(S): Heinicke, J.; Tzschach, A.

CORPORATE SOURCE:

Sekt. Chem., Martin-Luther-Univ. Halle-Wittenberg,
Halle/Saale, DDR-4020, Ger. Dem. Rep.

SOURCE:

Journal fuer Praktische Chemie (Leipzig) (1983),
325(2), 232-7

CODEN: JPCEAO; ISSN: 0021-8383

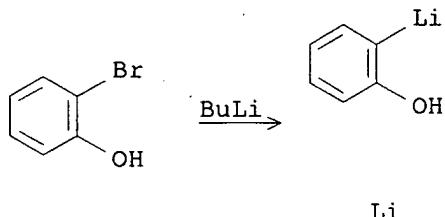
DOCUMENT TYPE: Journal

LANGUAGE: German

AB Approx. 10 arsino- and silylphenol derivs. and arsino- and

phosphinoanilides were prepared by the reaction of the title compds. with chloroarsines, chlorosilanes, and chlorophosphines. Thus, α -LiC₆H₄OLi and Me₃CAsCl₂ gave Me₃CAs(C₆H₄OLi- α)₂, which, with Me₃CSiCl, gave 60% Me₃CAs(C₆H₄OSiMe₃- α)₂. Similarly, α -LiC₆H₄N(Li)Me and ClP(NMe₂)₂ gave 72% α -(Me₂N)₂PC₆H₄[NMeP(NMe₂)₂]₂.

RX(2) OF 11



L6 ANSWER 41 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 99:158685 CASREACT

TITLE: Coenzymes Q

PATENT ASSIGNEE(S): Dainippon Ink and Chemicals, Inc., Japan; Kawamura Physical and Chemical Research Institute

SOURCE: Jpn. Kokai Tokkyo Koho, 7 pp.

CODEN: JKXXAF

DOCUMENT TYPE: Patent

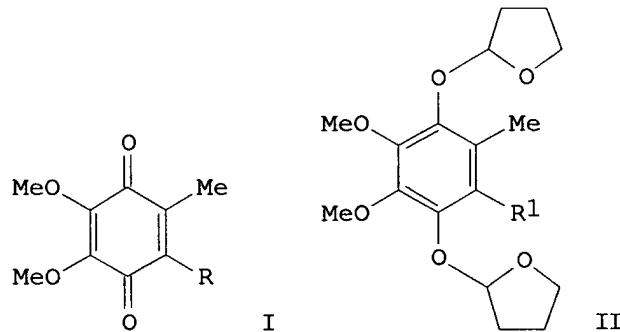
LANGUAGE: Japanese

FAMILY ACC. NUM. COUNT: 1

PATENT INFORMATION:

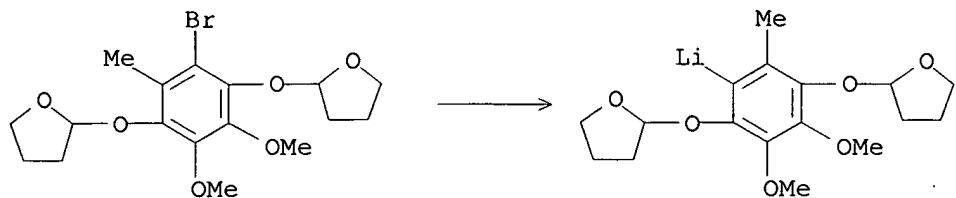
PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
JP 58041839	A	19830311	JP 1981-139669	19810907
PRIORITY APPLN. INFO.:			JP 1981-139669	19810907

GI



AB Title compds. (I, R = solanesyl, decaprenyl, geranyl, phytyl) were prepared by alkylation of II (R₁ = Li) with RBr and subsequent hydrolysis and oxidation. Thus, treatment of 350 mg solanesyl bromide in THF with II (R₁ = Li), obtained from 400 mg II (R₁ = Br), at -60° for 2 h and at -60 to 0° for 15 h gave 740 mg II (R₁ = solanesyl), whose acid hydrolysis followed by Ag₂O oxidation gave I (R = solanesyl).

RX(2) OF 5



L6 ANSWER 42 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 99:104903 CASREACT

TITLE: Regiospecific synthesis of aromatic compounds via organometallic intermediates. I. para-Substituted benzenes

AUTHOR(S): Chen, Loomis S.; Chen, Grace J.; Tamborski, Christ

CORPORATE SOURCE: Mater. Lab., Air Force Wright Aeronaut. Lab., Wright-Patterson Air Force Base, OH, 45433, USA

SOURCE: Journal of Organometallic Chemistry (1983), 251(2), 139-48

CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal

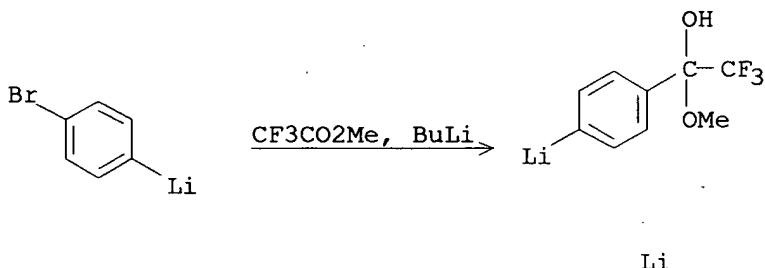
LANGUAGE: English

AB 4-RC₆H₄COCF₃ (R = H, Me, CO₂H, COMe, COCF₃, CHO, SH) were prepared by sequential metal-halogen exchange between 1,4-Br₂C₆H₄ and BuLi and electrophiles. Low reaction temperature is critical to stabilization of the various intermediates. The CF₃ group has a pronounced effect on stabilizing the Li hemiketal intermediates.

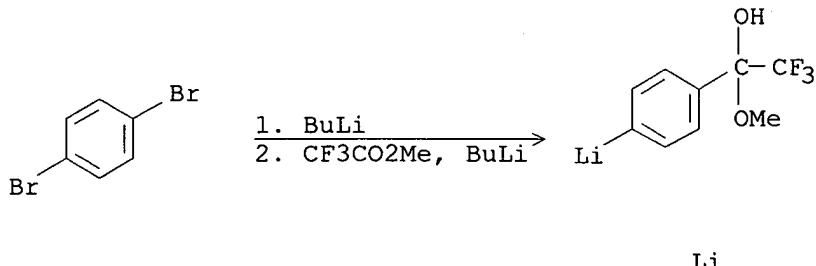
RX(2) OF 29



RX(11) OF 29



RX(13) OF 29 - 2 STEPS



L6 ANSWER 43 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 97:38583 CASREACT

TITLE:

Reactions of methylcopper and chiral organocuprates with 1-nitro-2-phenylethene and of lithium dimethylcuprate with methyl 3-(nitrophenyl)propenoates

AUTHOR(S): Hansson, A. T.; Nilsson, M.

CORPORATE SOURCE: Dep. Org. Chem., Chalmers Univ. Technol., Goteborg, S-412 96, Swed.

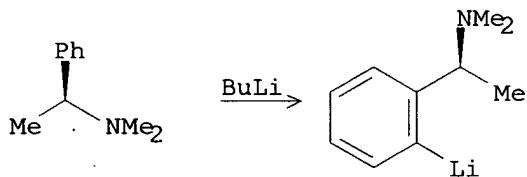
SOURCE: Tetrahedron (1982), 38(3), 389-91
CODEN: TETRAB; ISSN: 0040-4020

DOCUMENT TYPE: Journal

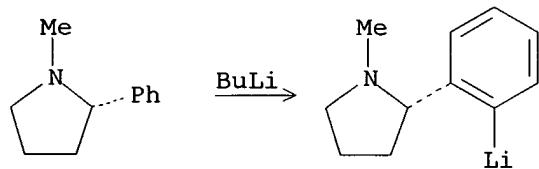
LANGUAGE: English

AB Organometallic compds., e.g. MeCu, LiCuMe₂, S-(2-Me₂NCHMeC₆H₄)CuMeLi (I), and Li menthoxymethylcuprate reacted with E-PhCH:CHNO₂ (II) to give PhCHMeCH₂NO₂ (III) in moderate yields. E.g., treatment of II with I in dry Et₂O at -40° gave 22% III with 2% enantiomeric excess. Treatment of p-O₂NC₆H₄CH:CHCO₂Me (p-IV) with LiCuMe₂ gave the corresponding azoxy compound, whereas m-IV with LiCuMe₂ gave some conjugate addition

RX(18) OF 97



RX(21) OF 97



L6 ANSWER 44 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 97:6353 CASREACT

TITLE:

Regioselective dimetalation of aromatic compounds. Easy access to 2,2'-disubstituted biphenyl derivatives

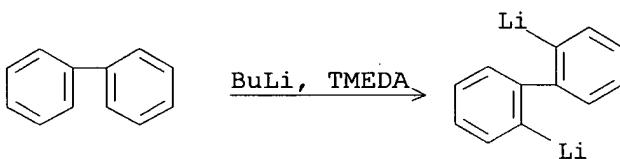
AUTHOR(S): Neugebauer, Wolfgang; Kos, Alexander J.; Schleyer, Paul von Rague

CORPORATE SOURCE: Inst. Org. Chem., Friedrich-Alexander-Univ.
 Erlangen-Nuernberg, Erlangen, D-8520, Fed. Rep. Ger.
 SOURCE: Journal of Organometallic Chemistry (1982), 228(2),
 107-18
 CODEN: JORCAI; ISSN: 0022-328X

DOCUMENT TYPE: Journal
 LANGUAGE: German

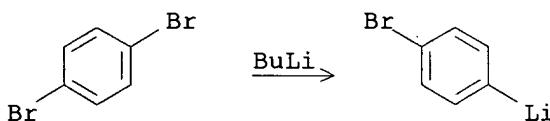
AB Lithiation of biphenyl with 2.4 mol BuLi in the hexane containing Me₂NCH₂CH₂NMe₂ gave 2,2'-dilithiobiphenyl(I) in modest, but preparatively useful yields. I was converted into a variety of products. The activation of the 2'-position of 2-lithiobiphenyl was shown directly by a sep. experiment MNDO calcns. indicate stabilization in I by double bridging and in 2-lithiobiphenyl by intramol. π -interaction of the Li atom with the o-Ph group. Similar interactions in substitution transition states rationalize the specificity of the reactions observed

RX(2) OF 10



L6 ANSWER 45 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 96:34746 CASREACT
 TITLE: Fluoro ketones. V. Reactions of alkyl and aryllithium compounds with perfluoroalkyl ether esters
 AUTHOR(S): Chen, Loomis S.; Tamborski, Christ
 CORPORATE SOURCE: Mater. Lab., Air Force Wright Aeronaut. Lab., Wright Patterson AFB, OH, 45433, USA
 SOURCE: Journal of Fluorine Chemistry (1981), 19(1), 43-53
 CODEN: JFLCAR; ISSN: 0022-1139
 DOCUMENT TYPE: Journal
 LANGUAGE: English
 AB BuLi and aryllithium compds. reacted with a perfluoroalkyl ether ester at -78° to produce perfluoroalkyl ether ketones. Steric hindrance adjacent to the carbonyl group has an important effect on rates of reactions. Low reaction temperature is an important factor when secondary esters are used. At >-30° the decreased yields of ketone was due to the instability of the intermediate Li salt of the hemiketal which decomposed to an aryl ester and a perfluorinated olefin.

RX(7) OF 18



L6 ANSWER 46 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 96:6277 CASREACT
 TITLE: Selective halogen-lithium exchange in some secondary and tertiary (bromophenyl)alkyl halides
 AUTHOR(S): Parham, William E.; Bradsher, Charles K.; Reames, David C.
 CORPORATE SOURCE: Paul M. Gross Chem. Lab., Duke Univ., Durham, NC, 27706, USA

SOURCE: Journal of Organic Chemistry (1981), 46(23), 4804-6

CODEN: JOCEAH; ISSN: 0022-3263

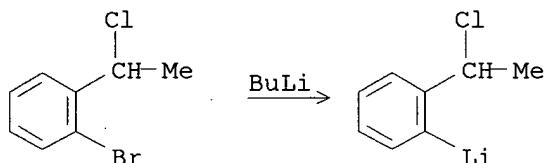
DOCUMENT TYPE: Journal

LANGUAGE: English

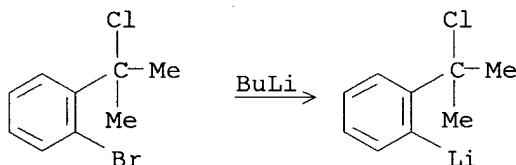
GI For diagram(s), see printed CA Issue.

AB At -100° I ($R = H, Me; R1 = Me$) undergo efficient selective Br^- -Li exchange to give the corresponding II which, like, II ($R = R1 = H$) [from I ($R = R1 = H$)], react with cyclohexanone to give an anion which cyclizes spontaneously to give III ($R = H, Me$); III ($R = H$) is formed in higher yield than III ($R = Me$). IV ($R = Me$), derived from V ($R = Me$) cyclizes more slowly and in poorer yield than does its analog IV ($R = H$).

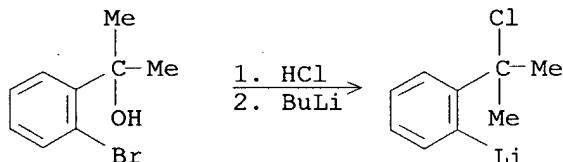
RX(7) OF 26



RX(8) OF 26



RX(15) OF 26 - 2 STEPS



L6 ANSWER 47 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 95:132382 CASREACT

TITLE: Regiospecific functionalization of unsaturated compounds via their dilithio derivatives. Part III. Synthesis of α -halophenylacetylenes via the dianion of phenylacetylene

AUTHOR(S): Hommes, H.; Verkruisje, H. D.; Brandsma, L.

CORPORATE SOURCE: Dep. Org. Chem., Univ. Utrecht, Utrecht, 3522 AD, Neth.

SOURCE: Tetrahedron Letters (1981), 22(26), 2495-6

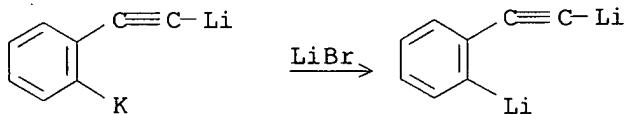
CODEN: TELEAY; ISSN: 0040-4039

DOCUMENT TYPE: Journal

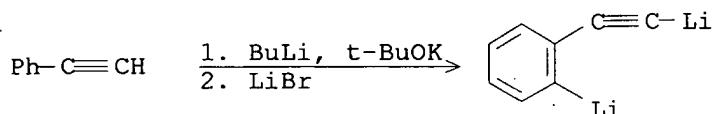
LANGUAGE: English

AB α - $RC_6H_4C.tpbond.CH$ ($R = iodine, Br, Cl$) were prepared by reaction of iodine, Br_2 , and C_2Cl_6 , resp., with α - $RC_6H_4C.tpbond.CR$ ($R = Li, BrMg$). E.g., treatment of α - $MgBrC_6H_4C.tpbond.CMgBr$ with 1 equiv iodine (THF, -60°) followed by aqueous workup gave 71% α - $IC_6H_4C.tpbond.CH$.

RX(8) OF 19



RX(11) OF 19 - 2 STEPS



L6 ANSWER 48 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 95:80631 CASREACT

TITLE: Lithiation reactions of 1-(2'-bromophenyl)pyrrole and related compounds

AUTHOR(S): Cartoon, M. E. K.; Cheeseman, G. W. H.

CORPORATE SOURCE: Dep. Chem., Queen Elizabeth Coll., London, W8 7AH, UK

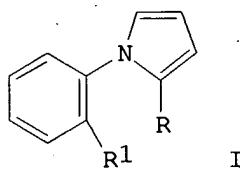
SOURCE: Journal of Organometallic Chemistry (1981), 212(1), 1-9

CODEN: JORCAI; ISSN: 0022-328X

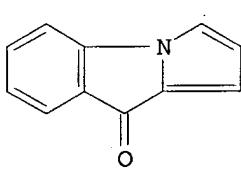
DOCUMENT TYPE: Journal

LANGUAGE: English

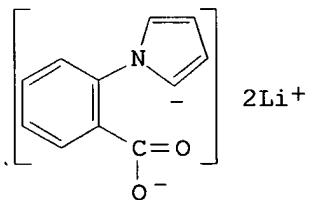
GI



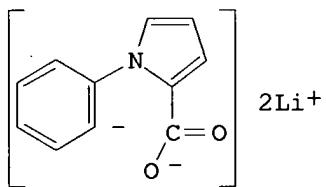
I



II



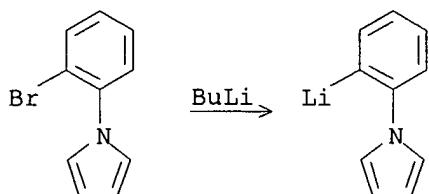
III



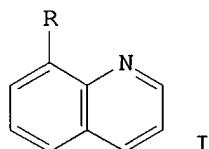
IV

AB Treatment of the phenylpyrroles I (R = H, R1 = CO2H; R = CO2H, R1 = Br) with LiN(CHMe2)2 or BuLi gave the pyrroloindolone II, presumably via the dilithio intermediates III or IV, resp. Reaction of the (lithiophenyl)pyrrole I (R = H, R1 = Li), generated from I (R = H, R1 = Br) and BuLi at -80°, with Ph2CO, BzH, BzCl, PhCN, EtO2CCl, and PhO2CCl gave I (R = H; R1 = CPh2OH, CHPhOH, COPh, CPh:NH, CO2Et, CO2Ph) in fair to good yields.

RX(7) OF 29



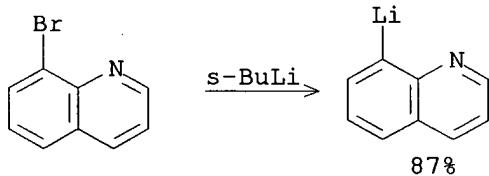
L6 ANSWER 49 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 92:215240 CASREACT
TITLE: Facile synthesis of 8-substituted quinolines
AUTHOR(S): Suggs, J. William; Pearson, G. D. N.
CORPORATE SOURCE: Bell Lab., Murray Hill, NJ, 07974, USA
SOURCE: Journal of Organic Chemistry (1980), 45(8), 1514-15
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
GI



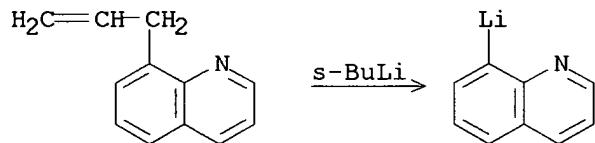
I

AB The title compds. I (R = CDO, CHO, CHMe(OH), CH₂CH:CH₂, PPh₂, Me, SnMe₃, CH₂CH₂OH) were prepared in 32-87% yields by lithiating I (R = Br) with MeEtCHLi to give I (R = Li) followed by treatment with the appropriate electrophile, e.g., MeI.

RX(2) OF 25

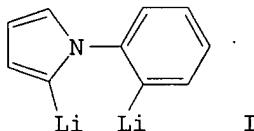


RX(3) OF 25



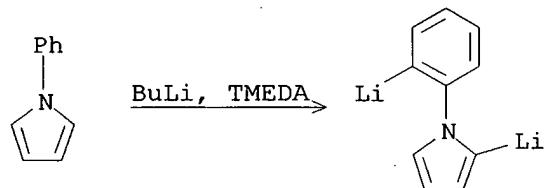
L6 ANSWER 50 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 90:168659 CASREACT
TITLE: Preparation and reactivity of 2,2'-dilithio-1-phenylpyrrole
AUTHOR(S): Cheeseman, G. W. H.; Greenberg, S. G.
CORPORATE SOURCE: Dep. Chem., Queen Elizabeth Coll., London, UK

SOURCE: Journal of Organometallic Chemistry (1979), 166(2), 139-52
CODEN: JORCAI; ISSN: 0022-328X
DOCUMENT TYPE: Journal
LANGUAGE: English
GI

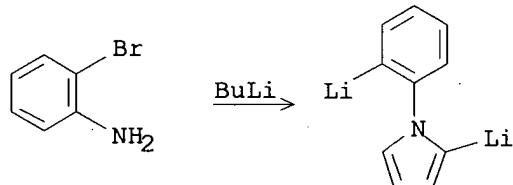


AB The title compound (I) was prepared by lithiation of 1-(2-bromophenyl)pyrrole with 2 equivalent of BuLi in ether at 0°. Some reactions of I were discussed. The benzenoid Li is more reactive towards electrophiles than the pyrrolic Li.

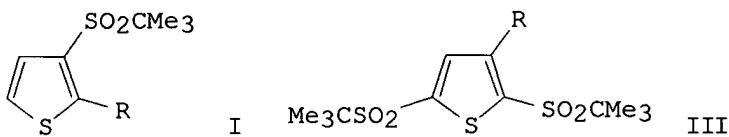
RX(1) OF 36



RX(2) OF 36

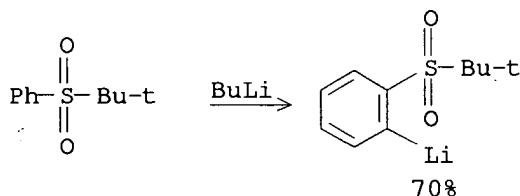


L6 ANSWER 51 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 90:151900 CASREACT
TITLE: Reactions of arylsulfonyl compounds with an excess of organolithium reagent. 13. Synthesis of o-mercaptosulfones and o-disulfones of benzene, naphthalene, and thiophene series based on o-lithiumsulfones
AUTHOR(S): Gol'dfarb, Ya. L.; Stoyanovich, F. M.; Chermanova, G. B.; Lubuzh, E. D.
CORPORATE SOURCE: Inst. Org. Khim. im. Zelinskogo, Moscow, USSR
SOURCE: Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya (1978), (12), 2760-7
DOCUMENT TYPE: Journal
LANGUAGE: Russian
GI

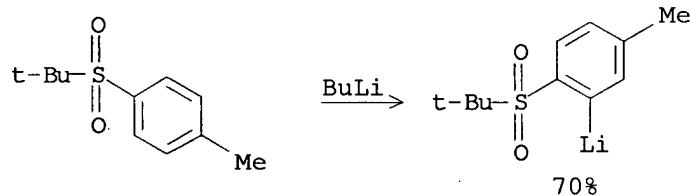


AB O-mercaptop sulfones of the benzene, naphthalene and thiophenes and their transition metal salts were prepared. The IR showed the existence of the intramol. H bond in the mercaptosulfones; it also confirmed the participation of the sulfonyl groups in coordination with the metal in their metallic derivs. A series of o-bissulfones and trissulfones of the benzene and thiophene series were prepared; one of these sulfonyl groups was the principal possibility for nucleophilic substitution. Mercaptan I ($R = SH$) (II) was obtained in 79% yield by reaction of I ($R = Li$) with S. II was converted to 30-63% I ($R = MeS, Me_3CS$) by reaction with the corresponding alkyl halides. The sulfides were oxidized to give 40.5-68% I ($R = MeSO_2, Me_3CSO_2$). Treatment of thiophene III ($R = H$) with $LiN(CHMe_2)_2$ at -40° followed by S gave 79.5% III ($R = SH$). III ($R = SO_2CMe_3$) was obtained by successive treatment of 3-tert-butylthio-2,5-dilithiothiophene with S, MeS and H_2O_2 in $AcOH$.

RX (5) OF 49

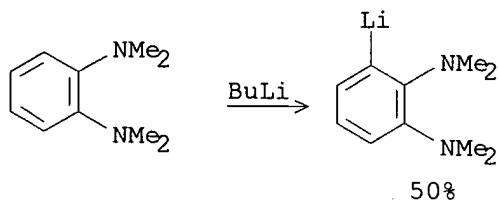


RX (6) OF 49

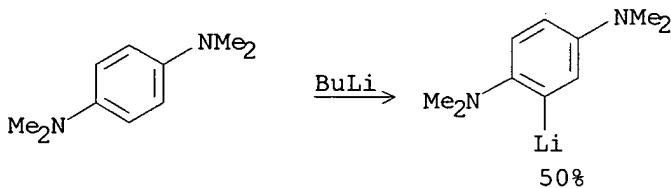


L6 ANSWER 52 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
ACCESSION NUMBER: 90:87536 CASREACT
TITLE: Metalation of aromatic tertiary diamines with
n-butyllithium
AUTHOR(S): Friedmann, Gilbert; Linder, Pierre; Brini, Mathilde;
Cheminat, Annie
CORPORATE SOURCE: Lab. Synth. Org., Inst. Chim., Strasbourg, Fr.
SOURCE: Journal of Organic Chemistry (1979), 44(2), 237-9
CODEN: JOCEAH; ISSN: 0022-3263
DOCUMENT TYPE: Journal
LANGUAGE: English
AB Lithiation of o- and p-(Me₂N)₂C₆H₄, and (p-Me₂NC₆H₄)CH₂ with BuLi in
hexane at 60° gave 2,3- and 2,5-(Me₂N)₂C₆H₃Li and [3,4-Li
(Me₂N)C₆H₃]₂CH₂, resp.

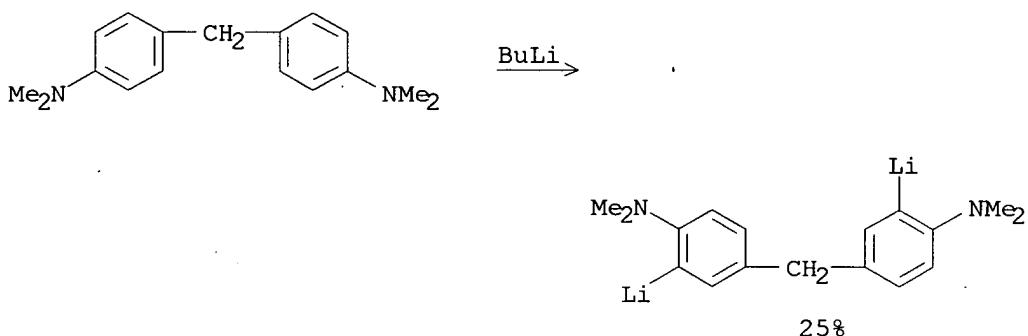
RX(1) OF 9



RX(3) OF 9



RX(5) OF 9



L6 ANSWER 53 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 85:46792 CASREACT

TITLE:

Lithiation of pyrido[*b*]cycloalkenes with phenyllithium

AUTHOR(S):

Epsztajn, J.; Bieniek, A.; Brzezinski, J. Z.

CORPORATE SOURCE:

Inst. Chem., Univ. Lodz, Lodz, Pol.

SOURCE:

Bulletin de l'Academie Polonaise des Sciences, Serie des Sciences Chimiques (1975), 23(11), 917-22

CODEN: BAPCAQ; ISSN: 0001-4095

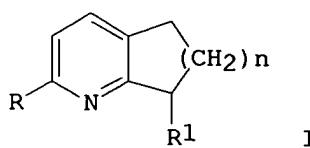
DOCUMENT TYPE:

Journal

LANGUAGE:

English

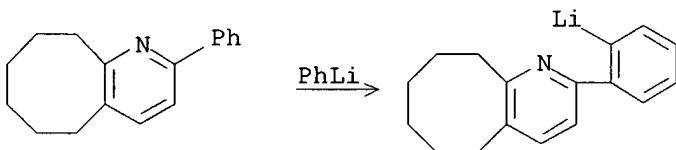
GI



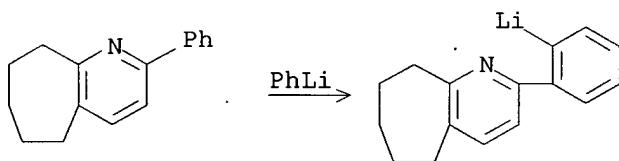
AB The direction of lithiation of pyrido[*b*]cycloalkenes I with PhLi in Et2O depended on the size of the cycloalkene ring. The relative reactivity of the C-H bond of the methylene group of the cycloalkene ring depends on the

ring size effect, i.e. $n = 2 > n = 1$ and $\text{Me} > \text{Ph} > n = 3 > n = 4$. I ($\text{R} = \text{Ph}$, $\text{R}1 = \text{H}$, $n = 1, 2$) and 6-phenyl-2-picoline gave I ($\text{R} = \text{Ph}$, $\text{R}1 = \text{Li}$, $n = 1, 2$) and 2-lithiomethyl-6-phenylpyridine, resp., and I ($\text{R} = \text{Me}$, $\text{R}1 = \text{H}$, $n = 2-4$) gave I ($\text{R} = \text{Me}$, $\text{R}1 = \text{Li}$, $n = 2$) and I ($\text{R} = \text{LiCH}_2$, $\text{R}1 = \text{H}$, $n = 3, 4$), resp. I ($\text{R} = \text{Me}$, $\text{R}1 = \text{H}$, $n = 1$) gave 1:1 I ($\text{R} = \text{Me}$, $\text{R}1 = \text{Li}$, $n = 1$) (II) and I ($\text{R} = \text{LiCH}_2$, $\text{R}1 = \text{H}$, $n = 1$) instead of the expected III. Lithiation of I ($\text{R} = \text{Ph}$, $\text{R}1 = \text{H}$, $n = 3, 4$) initially gave I ($\text{R} = \text{o-LiC}_6\text{H}_4$ $\text{R}1 = \text{H}$, $n = 3, 4$) which slowly rearranged to give I ($\text{R} = \text{Ph}$, $\text{R}1 = \text{Li}$, $n = 3, 4$).

RX(1) OF 4



RX(4) OF 4



L6 ANSWER 54 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 84:135202 CASREACT

TITLE: Selective halogen-lithium exchange in bromophenylalkyl halides

AUTHOR(S): Parham, William E.; Jones, Lawrence D.; Sayed, Yousry A.

CORPORATE SOURCE: Paul M. Gross Chem. Lab., Duke Univ., Durham, NC, USA

SOURCE: Journal of Organic Chemistry (1976), 41(7), 1184-6

CODEN: JOCEAH; ISSN: 0022-3263

DOCUMENT TYPE: Journal

LANGUAGE: English

GI For diagram(s), see printed CA Issue.

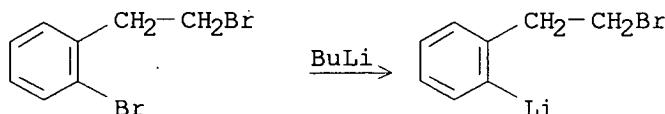
AB Exchange of the aryl halide atom in $\text{o-BrC}_6\text{H}_4\text{CH}_2\text{Cl}$, $\text{o-BrC}_6\text{H}_4(\text{CH}_2)_2\text{Br}$, and $\text{o-BrC}_6\text{H}_4(\text{CH}_2)_3\text{Cl}$ for Li was carried out with BuLi in THF-hexane at -100° . The stable lithio derivs. reacted with a variety of electrophiles; e.g., $\text{o-LiC}_6\text{H}_4\text{CH}_2\text{Cl}$ (I) with H_2O , cyclohexanone, or PhNCO at low temperature gave, resp., PhCH_2Cl , II, and III. I with H_2O at room temperature

gave 9,10-dihydroanthracene (not benzocyclopropene). Benzocyclobutene was formed from $\text{o-LiC}_6\text{H}_4(\text{CH}_2)_2\text{Br}$ under similar conditions. O-halobenzyl bromides were lithiated at the benzyl bromine atom and underwent subsequent coupling to bibenzyl. $\text{o-BrC}_6\text{H}_4(\text{CH}_2)_3\text{Br}$ with BuLi underwent intramol. coupling to indan.

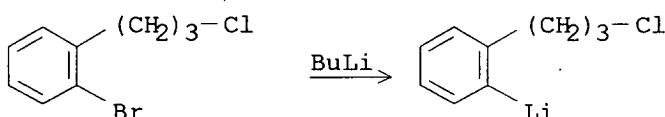
RX(4) OF 19



RX(6) OF 19



RX(8) OF 19



L6 ANSWER 55 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 67:11392 CASREACT

TITLE: The structure of a C₃₀H₂₆O₁₂ procyanidin from cola nuts

AUTHOR(S): Weinges, Klaus; Perner, Johannes

CORPORATE SOURCE: Univ. Heidelberg, Heidelberg, Fed. Rep. Ger.

SOURCE: Chemical Communications (London) (1967), (7), 351-2

CODEN: CCOMA8; ISSN: 0009-241X

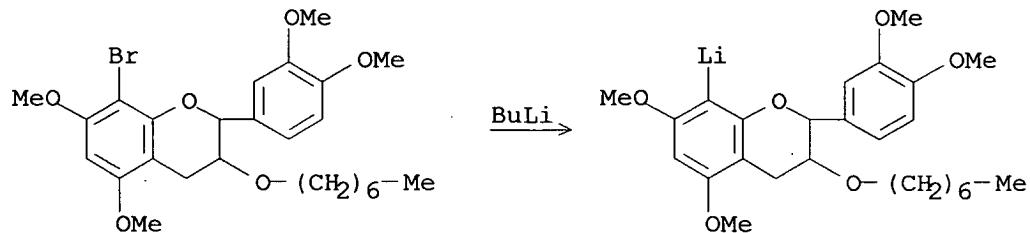
DOCUMENT TYPE: Journal

LANGUAGE: English

GI For diagram(s), see printed CA Issue.

AB cf. CA 63: 5588b. The structure of a procyanidin (I) isolated from cola nuts was confirmed by synthesis. Bromination of II (R = R' = H) gave II (R = Br, R' = H) which was benzylated to give II (R = Br, R' = PhCH₂) (III). Treatment of III with BuLi gave II (R = Li, R' = PhCH₂) which was condensed directly with IV followed by hydrogenolysis and acetylation to give I.

RX(1) OF 1



NOTE: Classification: Lithiation; Exchange; # Conditions: n-BuLi

L6 ANSWER 56 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 65:65119 CASREACT

TITLE: Steric effects in the metalation of some aromatic substrates with alkylolithium reagents

AUTHOR(S): Hendrix, John Paul, Jr.

CORPORATE SOURCE:

SOURCE:

Univ. of Tennessee, Knoxville

(1966) 158 pp. Avail.: Univ. Microfilms (Ann Arbor, Mich.), Order No. 66-5346

From: Dissertation Abstr. 26(12), 7036

DOCUMENT TYPE:

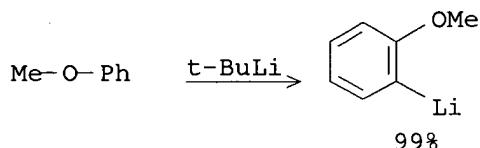
Dissertation

LANGUAGE:

English

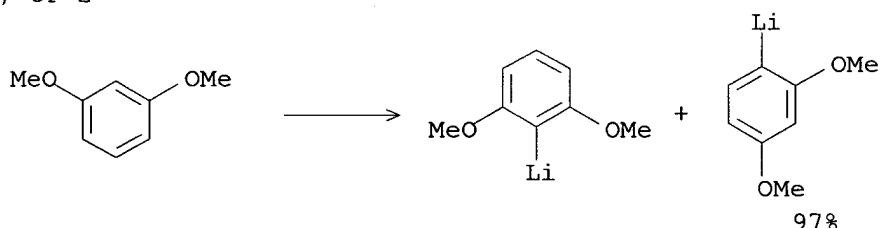
AB Unavailable

RX(1) OF 2



NOTE: Classification: Lithiation; Regioselective; # Conditions: t-BuLi

RX(2) OF 2



NOTE: Classification: Lithiation; Regioselective; # Conditions: n-BuLi; # Comments: 97% of yield is 1,2,3-substituted product; 3% of yield is 1,4,3-substituted product

L6 ANSWER 57 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

52:113367 CASREACT

TITLE:

Organotin compds. with bulky aryl groups. I.

Tetra(2-biphenyl)tin, and the 3- and 4-isomers

AUTHOR(S):

Bahr, Gerhard; Gelius, Rolf

CORPORATE SOURCE:

Univ. Greifswald, Germany

SOURCE:

Chemische Berichte (1958), 91, 812-18

CODEN: CHBEAM; ISSN: 0009-2940

DOCUMENT TYPE:

Journal

LANGUAGE:

Unavailable

AB An Et₂O-C₆H₆ solution (175 ml.) containing 13.7 g. (2-biphenyl)lithium (cf. Bell, et al., C.A. 20, 2848; Campbell, C.A. 45, 6595b; Littlejohn and Smith, C.A. 48, 1749i; Zaheer and Faseeh, C.A. 39, 2913) is added in 0.5 hr., while stirring, to a solution of 4 g. SnCl₄ and 25 ml. dry C₆H₆. After evaporation of 75-100 ml. of the solvent, the solution is stirred, refluxed, and

heated 2 hrs., hydrolyzed with Br water, separated, crystallized, dried, and recrystd. (boiling 1,2-C₂H₄) to produce a 71.2% yield of tetra(2-biphenyl)tin (I), m. 300-1°, insol. in Et₂O and petr.

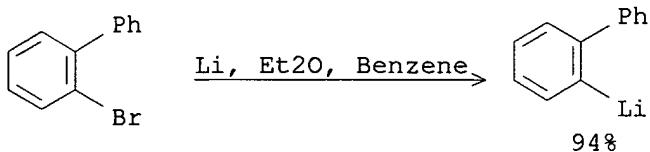
ether, hard to dissolve in hot AcOEt, EtOH, or tetrahydrofuran. I is the most stable of the 3 isomers. Tetra(3-biphenyl)tin (II) made similarly, m. 145.5-5.8°, somewhat soluble in Et₂O, soluble in C₆H₆, C₅H₆N, CHCl₃, hot AcOEt, and hot ligroine. II is the least symmetrical and lowest

melting of the 3. Tetra(4-biphenyl)tin (III), made in 77% yield, m. 268.5°, insol. in EtOH, difficultly soluble in Et₂O, easily in hot ligroine, hot AcOR, hot CHCl₃ and hot C₅H₅N. I and HgCl₂ react to form

(2-biphenyl)mercuric chloride, m. 166-7°. Di(2-biphenyl)tin chloride is produced by treating I with HCl. Tri(2-biphenyl)tin bromide, m. 107.5-8.0°, is made by treating (2-

biphenyl)magnesium bromide with SnBr_4 in a 4:1 molar ratio.

RX(1) OF 2



NOTE: Classification: Lithiation; Exchange; # Conditions: Li Et2O benzene; 1h; heat water bath; 1h-1h30mn

L6 ANSWER 58 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER: 52:104069 CASREACT

TITLE: Lithium sodium organic complexes. III. Anionization reactions with sodium diphenyllithium

AUTHOR(S): Wittig, Georg; Benz, Eberhard

CORPORATE SOURCE: Univ. Tubingen, Germany

SOURCE: Chemische Berichte (1958), 91, 873-82

CODEN: CHBEAM; ISSN: 0009-2940

DOCUMENT TYPE: Journal

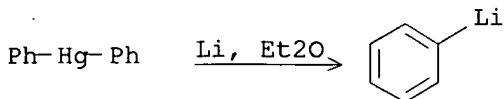
LANGUAGE: Unavailable

AB cf. C.A. 50, 1633d. Metalation reactions of CH_2Ph_2 and phenolic ethers were described which showed the superiority of $(\text{Ph}_2\text{Li})\text{Na}$ (I) over organic Li compds. and which confirmed the authors' conception that the mechanism was one of proton-metal exchange. Of particular interest was the conversion of Ph_2S to dibenzothiophene (II) in improved yields. (%) Metalation was determined by treatment with Ph_2CO . Ph_2Hg (m. 124°) (12 g.) in 50 cc. absolute Et2O (all operations under N) and 1.8 g. Li clippings and some glass fragments shaken 20 hrs. gave a 1.3N Et2O solution of PhLi (salt-free) (solution III); 20 cc. N III 3.6 g. Ph_2Hg in 110 cc. Et2O, 2 g. Na, and some broken glass shaken 2 hrs. gave a 0.15N solution of I (solution IV); 2 cc. N III, 3.6 g. Ph_2Hg , and 4.5 g. Na wire in 50 cc. absolute Et2O shaken 2 hrs. with glass fragments gave a suspension of I (1:10 PhLi-PhNa) (the suspension was decanted from the amalgam for use) (solution V). To 20 millimoles CH_2Ph_2 in 20 cc. absolute Et2O was added 66 cc 0.15N IV, the solution treated with Dry Ice after 90 min., and the product shaken with H2O to give 7% $\text{CHPh}_2\text{CPh}_2\text{OH}$ (VI), m. $229-30^\circ$ (EtOH) (as a precipitate), 61% CH_2Ph_2 , b12 $128-30^\circ$ (from the Et2O phase), 0.3 g. BzOH , and $\text{Ph}_2\text{C}(\text{CO}_2\text{H})_2$ (VII), m. $143-4^\circ$ (decomposition) (di-Me ester, m. 93°), converted by heating to $\text{CHPh}_2\text{CO}_2\text{H}$ (VIII), m. 146° . In a 2nd experiment, 10 millimoles CH_2Ph_2 in 10 cc. absolute Et2O and 33 cc. 0.15N IV

kept 16 hrs. under N, poured on Dry Ice, and worked up as above gave 26% VII and 23% VIII. In a 3rd experiment Ph_2CO added to the mixture after 16 hrs. gave 53% VI, 40% CH_2Ph_2 , Ph_2CO , and 25% Ph_3COH (IX). PhOMe (16 millimoles) and 8 millimoles IV in 63 cc. Et2O treated with 16 millimoles Ph_2CO after 3 hrs. (the Et2O boiled up), the mixture hydrolyzed, the Et2O removed, the residue extracted with petr. ether to remove Ph_2CO , and the remaining mixture (3.1 g.) chromatographed on Al_2O_3 gave, on elution with C_6H_6 , 23% $\text{o-MeOC}_6\text{H}_4\text{CPh}_2\text{OH}$ (X), m. $127-9^\circ$, and on further elution with CHCl_3 49% IX, m. $159-60^\circ$. A similar experiment in which Ph_2O was added after 48 hrs. gave 71% X. In a further experiment V (2 millimoles $\text{PhLi-20 millimoles PhNa}$) and 22 millimoles PhOMe in 50 cc. Et2O shaken 3 hrs. and treated with 20 millimoles Ph_2CO gave 40% X, m. $126-7^\circ$, and 46% IX, m. $158-9^\circ$. $\text{p-BrC}_6\text{H}_4\text{OMe}$ (16 millimoles) and 8 millimoles IV in 63 cc. Et2O treated with 16 millimoles Ph_2CO after 10 min., the mixture hydrolyzed, the Et2O phase worked up, and the residue

recrystd. from MeOH gave 1.1 g. [5,2-Br(MeO)C₆H₃]CPh₂OH (XI), m. 125-6°; the MeOH-soluble fraction chromatographed on Al₂O₃ in 1:10 C₆H₆-cyclohexane (XII) and eluted with the same solvent mixture gave 3% Ph₂C₆H₄-cyclohexane (XIII) and 5% 4-MeOC₆H₄Bz, m. 86-7° (petr. ether); continued elution with C₆H₆ gave 4% 4-MeOC₆H₄C₆H₄OMe-4, m. 170-2°, and 1.2 g. XI, m. 126-7°; further elution with CHCl₃ gave 11% IX and then 8% 4-MeOC₆H₄CPh₂OH, m. 78-9° (petr. ether-Et₂O). Ph₂S (20 millimoles) and 10 millimoles IV in 86 cc. Et₂O kept 20 hrs. at room temperature, treated with 20 millimoles Ph₂CO, hydrolyzed, the Et₂O phase distilled, unreacted Ph₂S (55%) distilled, and the residue chromatographed on Al₂O₃ gave 33% IX, m. 156-8°, 268 2-[Ph₂C(OH)]C₆H₄SPh (XIV), m. 142-3°, and 4.5% {2-[Ph₂C(OH)]C₆H₄S}₂ (XIV), m. 204.5-5.5°. XIII in boiling AcOH treated with a few drops of concentrated HCl cyclized and gave 10,10-diphenylthiaxanthine, m. 210-11° (EtOH). XIV treated similarly gave 4-(diphenylacetoxymethyl)-10,10-diphenylthiaxanthine, m. 306-8° (EtOAc). In a further experiment, 18 millimoles Ph₂S and 9 millimoles IV in 80 cc. Et₂O kept 4 days at room temperature and then heated at 60° for 4 days, the mixture decanted from precipitated NaH into H₂O, the Et₂O layer extracted with 20% aqueous NaOH (from the alkaline extract was isolated 90 mg. PhSH), the Et₂O distilled, and the residue pressed and recrystd. from EtOH gave 3.2 g. II, m. 97-8°. Ph₃N (18 millimoles) and 9 millimoles IV in 60 cc. Et₂O kept 2 weeks at room temperature (no separation of NaH observed), poured on Dry Ice, the reaction product extracted with Et₂O, and the extract distilled gave 82% recovered Ph₃N; the aqueous phase acidified gave 1 g. mixture which, after extraction of BzOH with XII, left 11% crude (2-HO₂CC₆H₄)₂NPh (XV), m. 223-4° (decomposition) (dilute EtOH). 2-PhNHC₆H₄CO₂H (XVI) (1.5 g.), 2.6 g. 2-IC₆H₄CO₂Me, 2 g. K₂CO₃, and 0.5 g. Cu (Naturkupfer C) in 1 cc. xylene heated 11 hrs. at 190°, the mixture extracted with dry Et₂O, boiled 30 min. with 10% aqueous KOH, the solution filtered, the filtrate acidified, and the precipitate recrystd. from HCO₂H gave 0.82 g. XV, m.p. and mixed m.p. 224-5° (decomposition). Similarly XVI and 3-IC₆H₄CO₂Me gave (2-HO₂CC₆H₄)(3-HO₂CC₆H₄)NPh, m. 224.5-5.5°, mixed m.p. with XVI depressed. Ph₃As (18 millimoles) and 9 millimoles IV in 60 cc. Et₂O kept 2 weeks at room temperature (NaH separated), hydrolyzed, filtered, the Et₂O layer distilled, the residue taken up in XII, chromatographed on Al₂O₃, eluted with XII (30% Ph₃As recovered), and then eluted with C₆H₆ gave 4% phenylbiphenylensarsine, m. 84-5° (EtOH). Anthracene (XVII) (7.4 g.) and 0.8 g. Mg turnings in 35 cc. tetrahydrofuran (XVIII) [dried over Ph₂CONa] treated after gentle warming with 1/4 of 5.3 g. o-FC₆H₄Br (m. -35°) in 15 cc. absolute XVIII under N, the remaining solution added dropwise with stirring after the initiation of the reaction while maintaining the temperature at 60°, boiled 90 min., the warm solution poured into MeOH (XVII precipitated), the solution evaporated (lastly in vacuo), the residue extracted twice with 50 cc. hot H₂O containing some HCl, filtered off and dried in vacuo, the solid in 45 cc. hot xylene boiled 20 min. with 5 g. maleic anhydride, and the product filtered off gave 7.8 g. adduct, m. 256-8°; the filtrate boiled 2 hrs. in 80 cc. 2N NaOH, washed, dried, and xylene removed gave 4.1 g. oily crystals (XIX); XIX digested with petr. ether (b. 50-70°), the residue (2.8 g.) dissolved in 70 cc. CCl₄, chromatographed on 280 g. acid Al₂O₃, and the CCl₄ removed gave 2.14 g. triptycene, m. 255.0-6.5° (from XII). The column then eluted with C₆H₆ gave 11% triphenylene, m. 194-5° (CCl₄). The mechanisms of these reactions are discussed.

RX(1) OF 3



NOTE: Classification: Lithiation; Transmetalation; # Conditions: Li
Et₂O /N₂ 20h; # Comments: product in 1.3N Et₂O solution

L6 ANSWER 59 OF 59 CASREACT COPYRIGHT 2008 ACS on STN

ACCESSION NUMBER:

52:1753 CASREACT

TITLE:

Dimerization of 4-isopropenylphenyl methyl sulfide
with 43% sulfuric acid

AUTHOR(S):

van der Zanden, J. M.; Nieuwenhuis, J.; Bos, H. J. T.

CORPORATE SOURCE:

State Univ., Groningen, Neth.

SOURCE:

Recueil des Travaux Chimiques des Pays-Bas et de la
Belgique (1957), 76, 669-73

CODEN: RTCPB4; ISSN: 0370-7539

DOCUMENT TYPE:

Journal

LANGUAGE:

Unavailable

AB C.A. 51, 11301c. On boiling with 43% H₂SO₄, 4-(CH₂:CMe)C₆H₄SM_e (I) dimerized more slowly than 4-(CH₂:CMe)C₆H₄OM_e (II) and about as rapidly as CH₂:CMePh under the same conditions. Filtered BuLi in Et₂O (from 137 g. BuBr and 18 g. Li in 2 l. absolute Et₂O) treated quickly with stirring with 89 g. p-BrC₆H₄SM_e in 800 ml. Et₂O, the mixture kept 15 min. at room temperature and cooled to 0°, treated dropwise in 25 min. with 60 g. Me₂CO in 100 cc. absolute Et₂O and the mixture kept 2 hrs., the suspension neutralized with 2N HCl and the Et₂O layer washed with aqueous NaHCO₃ and H₂O, the dried extract evaporated, distilled to remove 40 g. BuMe₂COH, b15 50-1°, and the residual crystalline mass recrystd. from MeOH gave 47 g. I, m. 49-50°. I (15 g.) boiled 7 hrs. with stirring with 130 ml. 43% H₂SO₄, the cooled mixture poured onto ice and extracted with Et₂O, the washed and dried extract evaporated, and the residue fractionated (N atmospheric) yielded 67%

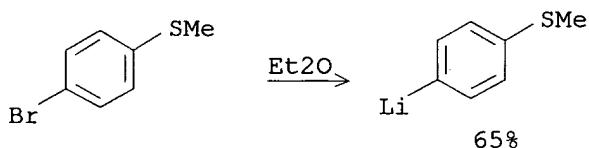
dimer (III), b4 256-8°, n₂₀D 1.6307. III (6 g.) in 600 ml. Me₂CO treated 1 week with 20 g. KMnO₄ with occasional shaking, the brown suspension filtered off, the filtrate evaporated, and the residual oil (3 g.) treated with 2,4-(O₂N)C₆H₃NHNH₂ in alc. H₂SO₄ to give authentic p-methylthioacetophenone 2,4-dinitrophenylhydrazone, m. 231.0-1.5°; the precipitate suspended in 50 ml. H₂O and clarified with SO₂, the warm solution filtered and cooled, filtered, and the crystalline precipitate (1.5 g.) crystallized from 50% alc. and twice from H₂O gave α-(p-methylsulfonylphenyl)isobutyric acid (IV), m. 182.3°. Condensation of MeSPh and ClCH₂OMe according to Buu-Hoi and Ho.acte.an (C.A. 47, 1634d) yielded 10.5% p-MeSC₆H₄CH₂Cl (V), b12 136-8°, n₂₀D 1.6051. V (10 g.) in 225 ml. 96% alc. refluxed 4.5 hrs. with 21.2 g. NaCN in 55 ml. H₂O and evaporated in vacuo, the residue diluted with 300 ml. H₂O and extracted with Et₂O, the dried extract evaporated, and the residue distilled gave 4.8 g. colorless liquid,

b1.0

118-31°, and material, b1.0 131-54°. Redistn. of the colorless liquid yielded 3.1 g. p-MeSC₆H₄CH₂CN (VI), b1.0 120.5-7.5°, n₂₀D 1.5827, ν 2240, 3450 cm.⁻¹ The latter band showed contamination of VI with p-MeSC₆H₄CH₂OH. Recrystn. of the semisolid material from petr. ether yielded 100 mg. pure VI, m. 40.5-1.5°, ν 2240 cm.⁻¹. VI (2.8 g.) in 10 ml. Et₂O added slowly with stirring to NaNH₂ (from 0.99 g. Na in 30 ml. Et₂O) and the mixture kept 2 hrs. at room temperature, the mixture refluxed 1.5 hrs. and cooled to

.. 0°, 3.35 g. MeI in 5 cc. Et₂O added and the mixture boiled 10 min., the cooled mixture treated with 3.35 g. MeI in 5 cc. Et₂O and refluxed 10 hrs., the mixture diluted with H₂O and extracted with Et₂O, the oily prod boiled 6 hrs. with 50 ml. HO(CH₂)₂OH, 2 ml. H₂O, and 2 g. KOH and the mixture poured into H₂O, the solution extracted with Et₂O and the extract treated with NaNO₂ and HCl, the extract washed with 2N NaOH and the alkaline washings added to the original KOH solution, the alkaline solution acidified and extracted with Et₂O, the pale brown oily product purified with 30% H₂O₂ in AcOH, and the colorless product recrystd. from H₂O gave 0.22 g. IV. A mechanism was proposed for the dimerization. I dimerized more slowly than II as a consequence of the pos. electromeric effect (+E), which is smaller with the MeS than with the MeO group. Since the +E effect of the MeSC₆H₄ group differs only slightly from that of the Ph group the rates of dimerization of I and CH₂:CMePh are almost identical.

RX(1) OF 1



NOTE: Classification: Lithiation; Exchange; # Conditions: n-BuLi Et₂O; 20 deg 15mn; # Comments: yield >65%

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---Logging off of STN---

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Executing the logoff script...

=> LOG Y

COST IN U.S. DOLLARS	SINCE FILE ENTRY	TOTAL SESSION
FULL ESTIMATED COST	493.96	494.17
DISCOUNT AMOUNTS (FOR QUALIFYING ACCOUNTS)	SINCE FILE ENTRY	TOTAL SESSION
CA SUBSCRIBER PRICE	-45.00	-45.00

STN INTERNATIONAL LOGOFF AT 11:19:48 ON 13 MAY 2008

L6 ANSWER 8 OF 59 CASREACT COPYRIGHT 2008 ACS on STN
 ACCESSION NUMBER: 127:5187 CASREACT <<LOGINID::20080513>>
 TITLE: Preparation of aryllithium in ether solutions using
 Lewis bases
 INVENTOR(S): Schwindeman, James A.; Sutton, Douglas E.; Morrison,
 Robert C.; Stryker, Sonia S.
 PATENT ASSIGNEE(S): FMC Corp., USA
 SOURCE: U.S., 4 pp.
 CODEN: USXXAM
 DOCUMENT TYPE: Patent
 LANGUAGE: English
 FAMILY ACC. NUM. COUNT: 1
 PATENT INFORMATION:

PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
US 5626798	A	19970506	US 1996-587813	19960105
WO 9725334	A1	19970717	WO 1996-US7624	19960524
W: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN RW: KE, LS, MW, SD, SZ, UG, AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG				
AU 9658036	A	19970801	AU 1996-58036	19960524
DE 19681729	T0	19981217	DE 1996-19681729	19960524
DE 19681729	C2	20001116		
PRIORITY APPLN. INFO.:			US 1996-587813	19960105
			WO 1996-US7624	19960524

OTHER SOURCE(S): MARPAT 127:5187

AB An improved process for producing high purity solns. of aryllithium compds. and the product solns. are claimed. The process comprises reacting a particulate alkali metal having a particle size of 10-300 μm , with an aryl halide in a normally liquid ethereal solvent ROR₁, wherein R and R₁ are selected from the group of alkyl radicals containing from 3 to 6 C atoms, in the presence of a Lewis base selected from compds. of the formula: R₂AR₃(R₄)_z and cyclic -(CR₅R₆)_y-(A(R₄)_z)- wherein A is selected from O, N, P or S; R₂, R₃, and R₄ are selected from alkyl radicals containing from 1 to 6 C atoms; R₅ and R₆ are independently selected from H or alkyl radicals containing one to six C atoms; y = 4 to 6; but when A is O or S, z = 0; and when A is N or P, z = 1, and provided there is a mole ratio of ether to aryl halide of at least 1.3 to 1 and a mole ratio of Lewis base to aryl halide of from 0.01 to 0.5. For example, to a reaction flask containing 1.25 mol Li powder and 0.94 mol Bu₂O was added, dropwise, over a period of 60 min, a solution of 0.52 mol PhCl and 0.052 mol MeOtBu, while maintaining the reaction temperature at 30-35°; the yield of PhLi was 87.4%. If no MeOtBu was present, the yield was 80.8% and the reaction was slower (16% PhCl remaining after 120 min vs. 6%).

RX(1) OF 1

